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CONTENTS

	PAGE
Special Steels for the Petroleum Industry. By R. Jackson and R. J. Sarjant, O.B.E.	445
Some Modifications of the Lamp Method for the Determination of Sulphur in Petroleum Products. By George E. Mapstone.	486
The Two-stage Ignition of Higher Hydrocarbons at Atmospheric Pressure. By G. Friedlander and L. Grunberg	490
Obituary: Alfred Courthope Adams	511
William A. Peters, Jr.	512
William Robert Guy	513
Abstracts	185A
Books Reviewed and Received	210A
Applications for Membership or Transfer and New Members	i–iii

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SPECIAL STEELS FOR THE PETROLEUM INDUSTRY.*

By R. JACKSON † and R. J. SARJANT,† O.B.E.

SUMMARY.

The paper reviews the major factors operative in the selection of special alloy steels for the petroleum industry. The heat- and corrosion-resisting properties of these steels are shown to improve with specific additions of alloying elements. The determination of optimum compositions, methods of fabrication, and conditions of service by an extension of statistical examination of behaviour in service trials is recommended. The significance of the effect of method of fabrication and heat treatment of the steels must be appreciated by the user, especially where alterations or repairs are carried out "in situ." The increasing importance of high quality castings, the fabrication being based on the application of radiographic examination, is also stressed.

THE many and varied purposes to which steel can be put in the petroleum industry, with their widely differing conditions of service, require correspondingly wide variations in the types of steel. It is impossible in a limited space to consider in detail all these variations, but the present paper shows the general trends in the types of steel which are suitable for the industry in situations in which corrosion, heat resisting, or other special properties are required.

These properties are imparted in two ways: by the additions of certain elements to the steel and by controlling the treatment to which it is submitted. Steel consists essentially of iron with a small addition of carbon and usually varying amounts of other elements such as sulphur, phosphorus, manganese, silicon, etc. The amount of carbon is a significant feature in all considerations of the properties of steel, even of the highly alloyed types. A mild steel of carbon content 0·25 per cent has a yield point of approximately 18 tons/sq. in, a maximum stress of 35 tons/sq. in, with an elongation of 20 per cent. It can be hardened up to a Brinell hardness of 300. It corrodes comparatively easily under most atmospheres and in contact with most materials. At temperatures of upwards of 350° C its mechanical strength is greatly reduced, and its creep resistance, *i.e.*, its resistance to extension under a small sustained load, is low. It also scales heavily at these high temperatures.

Very marked improvements of the properties of steel necessary for specific purposes are possible by the addition of certain combinations of the elements, chromium, nickel, tungsten, molybdenum, vanadium, titanium, niobium, etc. Notable amongst these properties are corrosion and heat resistance. As may be expected all the properties required for any one purpose are not obtained in any one material, nor may a particular material be suitable for a required purpose without suitable preparation (for example, heat treatment). Indeed, maltreatment may even produce results

* Paper read before Stanlow Branch, Institute of Petroleum, on March 4, 1947.
† Research Department, Messrs. Hadfields Ltd., Sheffield.

which are inferior to those obtainable from less specialized materials. Further, the properties which may be required, such as resistance to deformation at high temperatures in a heat-resisting steel, may entail difficulties in fabrication. Harder and tougher steels are less readily machined; in castings, for example, one of the most useful elements in conveying resistance to scaling, namely aluminium, introduces considerable difficulties in producing a satisfactory article.

Effect of Alloys on Heat Treatment.

The two main alloys which are introduced are chromium and nickel. These elements affect the heat-treatment and hardening properties of the steels, which have a pronounced effect in determining the possible use of the steel in service.

The behaviour of plain carbon steels on heat treatment can be determined by the aid of the iron–carbon equilibrium diagram (Fig. 1),[1] but the manner

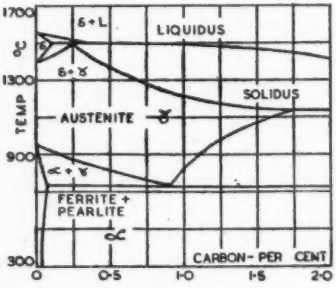

Fig. 1.

IRON–CARBON EQUILIBRIUM DIAGRAM. (AFTER THUM.)

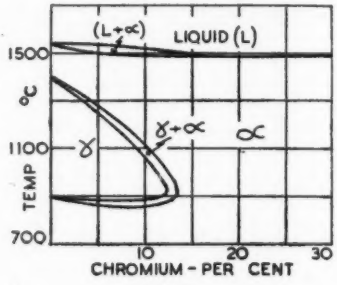

Fig. 2.

IRON–CHROMIUM EQUILIBRIUM DIAGRAM. (AFTER THUM.)

in which the separating phases are enabled to determine the structure of the steel depends upon the rate of cooling as well as the temperature of treatment. Thus, for example, in a 0·5 per cent carbon steel, the austenite cooled rapidly or quenched from 1200° C breaks down, the γ-iron changes to α-iron, but the carbide is unable to migrate and remains in the iron lattice, distorting it, setting up stresses and producing a macroscopically homogeneous mass known as martensite. These transformations are the basis of the hardening properties of the steel. When martensite is heated at temperatures up to about 700° C, the material becomes softer and more ductile or tempered. These changes are associated with the carbide migrating from the lattice.

Effect of Chromium.

The effect of chromium is shown in Fig. 2.[2] Carbon is assumed to be absent, and it will be seen that the addition of increasing amounts of chromium reduces the temperature range during which the iron is in the γ state. Above approximately 14 per cent chromium the iron is entirely in the α condition; that is, rapid heating and cooling in this range causes

no change in the structure, and heat treatment with consequent appreciable hardening or softening is not possible.

Effect of Nickel.

The reverse effect is obtained with nickel as shown in Fig. 3 [3] in which beyond 22 per cent the iron–nickel solution is entirely in the γ state. Again no change of phase occurs on cooling, and heat treatment produces no appreciable alteration in hardness. Solid solutions either of carbon, chromium, or nickel in α-iron are referred to as martensitic or ferritic, depending on the heat treatment, whereas solutions in γ-iron are referred to as austenitic.

When both chromium and nickel are present in addition to iron and carbon, the effect is more complex and it is difficult to represent the changes in structure in a diagram. The basic effects may be understood by considering the chromium as conducing to the formation of an α structure and

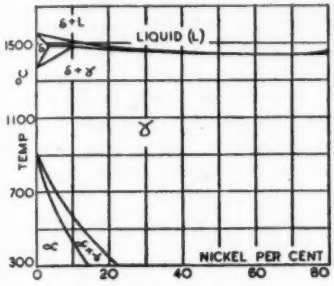

FIG. 3.

IRON–NICKEL EQUILIBRIUM DIAGRAM. (AFTER MARSH.)

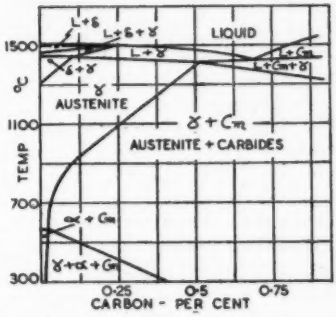

FIG. 4.

EFFECT OF CARBON ON CONSTITUTION OF 18 PER CENT CHROMIUM, 8 PER CENT NICKEL STEEL.

the nickel to a γ form. That this is not the whole story, however, is shown in Fig. 4,[4] which shows the influence of carbon on the structure of the usual 18 per cent chromium–8 per cent nickel alloy. The composition of such a mixed alloy will depend not only on the relative amounts of chromium and nickel present, but also on the amount of carbon.

In certain cases the austenite may exist in an unstable form, when the effect of heat treatment or slight changes in carbon content resulting from local segregation or migration of carbon may cause the ferritic state to appear or carbide to be precipitated. These effects have a pertinent practical influence, and are considered later under the 18/8 type of alloy.

In this paper emphasis is laid on three main properties of industrial importance, namely corrosion resistance, heat resistance, and mechanical properties at high temperatures, *i.e.*, creep and tensile strength.

CORROSION AND SCALING.

Probably one of the most important problems in the petroleum industry, especially in the refining stages, is that of corrosion, although this problem

does not attain the dimensions that it does in other branches of the chemical industry. Scaling is also of special importance in cracking plants.

Causes of Corrosion.

Corrosion can be divided into two types, electro-chemical and direct chemical attack. The former occurs in the presence of liquids, particularly water, at comparatively low temperatures up to about 250° C, while the latter takes place in the dry state at these and higher temperatures. Although the two types are produced by different kinds of mechanism they display some features of similarity, but it may be well to consider the two separately in the first place.

Electro-chemical Corrosion. If a piece of copper and a piece of zinc are placed in contact, a flow of electrons takes place from the zinc to the copper until the potential resulting is sufficient to oppose the flow. If the two unconnected ends of the two metals are now joined by means of a conducting liquid such as brine, the flow of electrons can take place from the copper to the zinc through the liquid, the potential is reduced and the electrons can flow again from the solid zinc to the copper and the current is maintained. At the liquid surface in contact with the zinc, the zinc atoms, which have been deprived of their electrons by the flow to the copper and so have become electro-positive, attract the negative ions of chlorine in the brine solution and form zinc chloride, which is soluble in the liquid and so becomes dispersed throughout it. At the same time the positively ionized sodium ions in the liquid are neutralized by the electron excess at the copper–liquid surface and become free sodium, which dissolves in the water producing caustic soda and hydrogen. The latter is evolved as a gas, and the former dissolves in the liquid and becomes dispersed. The dispersed products, zinc chloride and caustic soda, react together and form a precipitate of zinc hydroxide. There is nothing in this reaction which will prevent it from continuing and the zinc will ultimately be corroded entirely away. Various ways have been suggested for overcoming this type of corrosion, such as the use of a second anode connected electrically to the mass so that it is corroded preferentially to the zinc. This has been used successfully for protecting gas piping in Staffordshire, as reported by Jeavons and Pinnock.[5] Other ways of preventing corrosion by suitable imposition of electrical currents require skill and experience in the arrangement, but are of considerable practical importance, for example in the control of corrosion in pipelines.[6] Other possibilities may occur. Thus it might be that the salt produced at the zinc–liquid surface was not soluble in the liquid. In this case it would act as a barrier to the approach of the liquid and would reduce the rate of the attack. If the layer were an electrical non-conductor the circuit would eventually become broken and the action would cease. If the layer, however, were a conductor, the electrolytic action would take place at the surface of the layer, no reaction with the layer would occur and the final products would be those due to electrolysis of the water of the liquid, namely hydrogen and oxygen. Clearly such a film on the zinc would be beneficial to its corrosion resistance. If the protecting layer could drop off or be removed from the metal, the corrosion would again begin. Hence the nature of the layer and mechanical factors, such as turbulence in the liquid,

are of importance in corrosion in addition to the type of corroding medium.

Direct chemical Attack. The usual way in which this is met is in the action of scaling, and the discussion will be limited to this aspect.

It has been shown by Vernon [7] that oxidation proceeds in a series of discrete steps corresponding roughly to the stages : (*a*) formation of a layer of oxide which is one unit cell in thickness over the whole of the surface. When this has occurred there is (*b*) a change in the rate of oxidation as the metal and oxygen have now to pass to each other through the layer of oxide. Naturally the rate falls off with the increase in resistance, and a parabolic time–oxidation curve is obtained. In the oxide layer on iron there is, as shown by Pfeil,[8] a continual variation in the composition of the scale as the iron passes through the scale to meet the oxygen, the outer layers being Fe_2O_3 saturated with oxygen, and the inner layers FeO saturated with iron. Naturally, the closer the texture of the scale the more will it resist the penetration of the metal and the oxygen and thus the rate of attack. The initial stages of scaling are not yet quite clear. Uhlig [9] suggests that the first stage, before the formation of the oxide-unit cell, is the covering of the whole surface by a mono-atomic layer of adsorbed oxygen. Jackson and Quarrell [10] found, by means of the electron-diffraction camera, that at temperatures above about 500° C the initial oxide formed is not the FeO, which is stable at these temperatures, but an oxide with a hexagonal cell which is presumably a lower oxide than FeO, which may be growing pseudomorphically upon the Fe lattice. This would presumably be the next stage beyond the oxygen layer of Uhlig. This oxide would have a structure between that of Fe and FeO, and would act as a cement to hold the FeO in place. At temperatures over 900° C and below about 400° to 500° C the FeO is no longer stable, changing to Fe_3O_4 or Fe_2O_3; also at the intermediate temperatures an excess of oxygen might lead to these oxides being formed. As they are no longer even approximately pseudomorphic with iron a strain will be set up between the iron matrix and the scale layer, eventually causing the latter to flake away. It is a matter of experience that the scale forms in this manner, the rate of formation falling off with time as the thickness increases until the limiting thickness is reached when the scale flakes away, the thickness of the protection is reduced, and the rate of scaling increases again to be followed by a second gradual diminution in the rate. This scaling can also be caused, of course, by variations in the temperature exceeding the limits of the FeO-stable range. For these reasons scaling proceeds in a series of steps and scaling tests taken on a short-time basis are unreliable, as measurements may have to be taken just before or after flaking has occurred. In the results which are given later the tests were all carried out over a period of 3000 hours, except in those cases where the rate of attack was so high that the steel was clearly outside the range of the others being tested.

The theory put forward by Uhlig is interesting as giving an explanation of the scale resistance of certain steels. The unit-cell layer of Vernon may form an impervious coating for the metal, as in the case of aluminium, or the mono-atomic layer of Uhlig could be an explanation in certain cases. If, as he says, the oxygen layer forms and then combines with the metal by virtue of the free-valency bonds in the surface, we have an explanation of

the passivity of the chromium steels, for the free-valency electrons of the iron–chromium alloys would be reduced to zero for a composition of approximately 15 per cent Cr. In view of curves to be shown later, this is of interest.

However, it may be, as stated by several authors, that the resistance of the chromium alloys is due to the preferential oxidation of the chromium and the formation of a protective layer of the chromium oxide. In this connexion, the recent work of Hickman and Gulbransen [11] with the electron-diffraction camera indicates that the oxide formed on the lower-chromium alloys is a spinel of the iron and chromium oxides. This gives place above a content of 1 per cent Cr to the oxide of chromium only and reverts back to a spinel at the 13 per cent Cr alloy. The reason for this variation in composition is not known.

With scaling, as with electrolytic corrosion, the process can be increased by mechanical means which impair the continuity of the film or layer, and by increasing the rate of supply of the oxygen to the surface.

Although throughout the above reference has only been made to the action of oxygen, it will be clear that the formation of other products, such as, for example, sulphides, will result in similar types of attack. The reason for the increase in the rate of corrosion in a sulphur-laden atmosphere can be ascribed to the alteration in the composition of the scale, resulting in a more open structure allowing greater ease of penetration by the gases or by the metallic ions. This effect is more pronounced if the sulphur is in a reducing atmosphere, as it then controls the type of scale to a greater degree than if the oxide also tends to form as in an oxidizing atmosphere. This effect is indicated in the tests to be discussed later. Further, with two or more compounds, eutectics, as of FeS and FeO, may be formed, and these complicate the reactions and may result in increased activity.[12]

Laboratory and Service Tests.

Large numbers of experiments have been carried out both in the laboratory and in service on the corrosion of steel under widely varying conditions, and some of these results have been collected and studied here to show the effect of varying alloying elements.

In these tests it is appreciated that laboratory experiments may not be a true guide to performance in service, because usually the conditions in service are variable and to some extent unknown. In a particular problem investigated recently it was found that the conditions specified by the plant management caused little or no corrosion, whereas the material in service was highly corroded. On investigation it was found that an impurity in the processed material considered to be present in negligible amounts was actually present in amounts up to 2 per cent and the temperature of the metal was vastly in excess of that registered on the control instruments. Alteration of the operative factors reduced the corrosion to the expected figure.

However, with these considerations in mind, the results of laboratory and service tests can be usefully compared.

The most beneficial alloying element for reducing the corrosion of steel is chromium. Fig. 5 gives the results of experiments carried out in the Research Department of the authors' firm on the corrosion of various types

of steel in an industrial atmosphere after exposure for 12 months. The corrosion depends to a certain extent on the particular heat-treatment condition of the steel, but the results of tests on 70 different steels of varying composition shown in Fig. 5 are a sufficiently clear indication of the con-

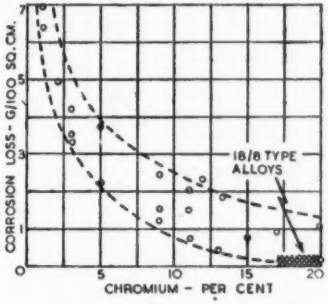

FIG. 5.

INFLUENCE OF CHROMIUM ON RESISTANCE TO CORROSION IN INDUSTRIAL ATMOSPHERE—12 MONTHS' EXPOSURE TESTS IN ATTERCLIFFE.

Plotted from 70 tests on steels varying in carbon, silicon, and chromium, and also varying heat treatment. Superimposed are tests on 18/8 (Cr 17 to 20; Ni 7 to 9) in same atmosphere and also covering usual additions of Ti, Mo, W, Cu, Nb, (Cb).

trolling effect of chromium in reducing susceptibility to this type of corrosion. The effect of additions of nickel are shown also in the 18 per cent chromium range, where the addition of 8 per cent nickel has a pronounced beneficial effect. This is also shown in Table I, where it is seen that other additions also

TABLE I.

Corrosion Tests—12 Months' Exposure to Industrial Atmosphere (Sheffield).

Material.	Corrosion loss Mild steel—100·0.
Mild steel	100
1% Cr steel	78
3% „	40
5% „	35
9% „	19
13% „	14
18% „	5·5
18 : 8. Cr : Ni . . .	1·5
18 : 8 : 1. Cr : Ni : Ti . .	1·5
18 : 8 : 3. Cr : Ni : Mo . .	0·5

have their effects. The effect of Ni alone, in resisting corrosion of hydrochloric nitric, and sulphuric acids, is shown in Figs. 6, 7, and 8.[13]

Pollock, Camp, and Hicks [14] have given results of a large number of tests on different materials met with in the petroleum industry. The tests were carried out under semi-service conditions, as the specimens were placed in the actual corrosive media in the plant. The relevant parts of the data are collected in Table II, and particular sections of this are shown in Figs. 9, 31,

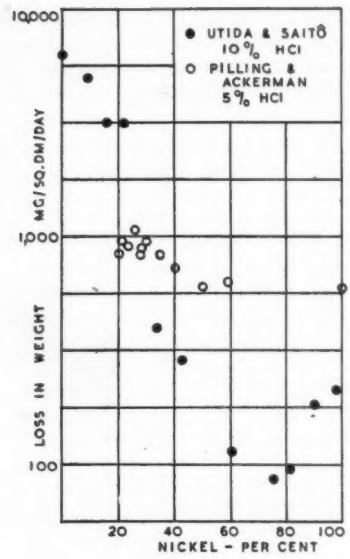

FIG. 6.

EFFECT OF NICKEL ON CORROSION RESISTANCE IN STEEL EXPOSED TO HCl. (AFTER MARSH.)

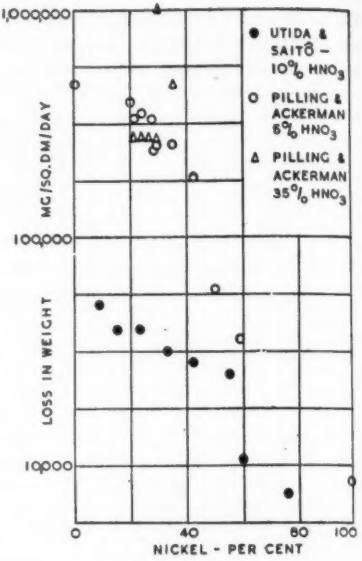

FIG 7.

EFFECT OF NICKEL ON CORROSION RESISTANCE IN STEEL EXPOSED TO HNO_3. (AFTER MARSH.)

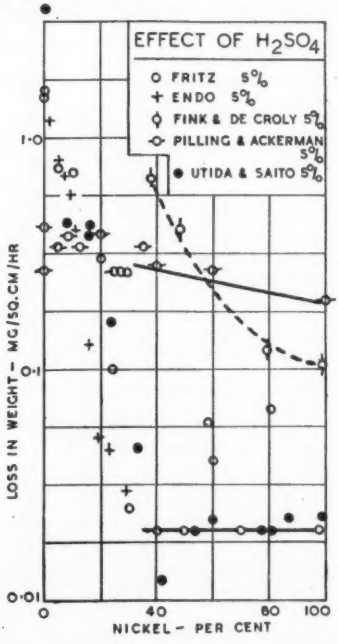

FIG. 8.

EFFECT OF NICKEL ON CORROSION RESISTANCE IN STEEL EXPOSED TO H_2SO_4. (AFTER MARSH.)

and 32. Fig. 9 shows the effect of chromium contents on resistance to attack by sea-water. This is of interest as sea-water is quite commonly used for

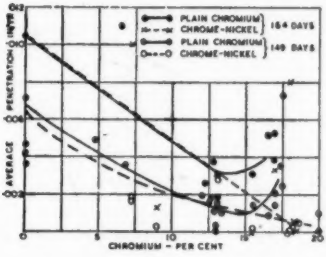

FIG. 9.

INFLUENCE OF CHROMIUM ON CORROSION IN CONDENSER BOXES (SALT WATER). (AFTER POLLOCK, CAMP, AND HICKS.)

cooling condensers. The effect of chromium is clear up to approximately 14 per cent, when further additions appear to give little further improvement. The addition of nickel to these high chromium steels appears to

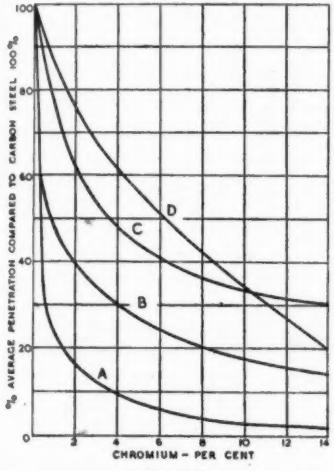

FIG. 10.

INFLUENCE OF CHROMIUM ON CORROSION IN REFINERIES. (AFTER WRIGHT.) A: SERVICE TESTS IN EVAPORATORS—VAPOUR PHASE; B: IN OIL CRACKING TUBES—LIQUID PHASE; C: IN OIL REACTION CHAMBERS—LIQUID PHASE; D: HYDROGEN SULPHIDE TESTS—168 HOURS AT 850° F.

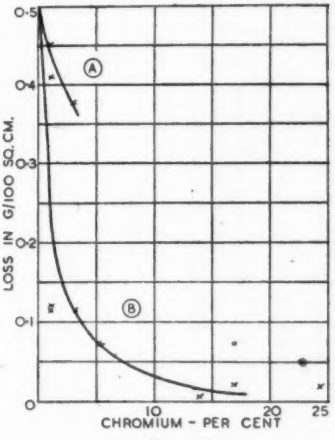

FIG. 11

INFLUENCE OF CHROMIUM ON CORROSION BY HIGH-PRESSURE STEAM CONTAINING H_2S. (SPECIMENS 2 INCH DIA × 2 INCH LONG.)

have an additive beneficial effect, however, and the corrosion is still further reduced. The effect of time on the corrosion is clearly seen in the figure.

The results of service tests carried out in eight different petroleum-refining plants have been reported by Wright [15] and are shown in Fig. 10.

Table II.

Results of Corrosion Tests in Various Media at a Petroleum Refinery.
(See Pollock, Camp, and Hicks.[14])

Strip no.	Type of steel.	Composition.								Average penetration, inches per year.						
										1	2	3	4	5	6	7
		C.	Si.	Mn.	Cr.	Ni.	Mo.	Fe.	W.	Fresh water.	Salt water condenser box.	Salt water condenser box.	Steam.	Crude-oil vapour.	Naphtha (liquid).	Cracking coil bubble tower.
							Carbon Steels.									
35	O.H. pickled	0·04	0·002	0·36	—	—	—	—	—	0·0129	0·0105	0·0073	0·0031	0·0529	0·0056	0·0171
46	Bessemer pickled	0·26	0·012	0·54	—	—	—	—	—	0·0119	—	0·0041	0·0034	0·0339	0·0054	0·0124
204	Standard	0·12	0·028	0·5	—	—	—	—	—	—	—	0·0046	—	0·0388	0·0530	0·0132
203	Standard	<0·25	—	0·3/0·5	—	—	—	—	—	0·0002	—	0·0036	—	0·0378	{0·0225 0·0353}	0·0122
70	Cast Iron	2·61	1·75	0·95	—	—	—	—	—	0·0005	—	0·0044	0·0089	0·0136	0·0111	0·0054
							Chromium Steels.									
109	4–6% Cr	0·18	0·019	0·35	4·85	—	—	—	—	0·0085	0·0039	0·0049	0·0024	0·0053	0·0048	0·0115
129	4–6% Cr	1·35	—	—	6·55	—	—	—	—	0·0003	0·0112	0·0035	0·0034	0·0038	0·0039	0·0101
15	12–14% Cr	0·11	0·282	0·4	13·14	0·196	—	—	—	nil	0·0030	0·0016	nil	0·0009	0·0047	0·0001
22	12–14% Cr	0·11	—	—	12·95	0·2	—	—	—	0·0010	0·0019	0·0011	0·0003	0·0021	0·0037	nil
30	12–14% Cr	<0·12	<0·5	0·2/0·4	11·5/13	<0·1	—	—	—	nil	0·0026	0·0019	0·0002	0·0016	0·0038	0·0004
64	12–14% Cr	0·07	0·1	0·28	12·75	0·27	—	—	—	,,	0·0038	0·0017	nil	0·0013	0·0050	0·0005
75	12–14% Cr (annealed and pickled)	0·07/0·12	<0·4	0·4/0·6	12/13	0·4/0·5	—	—	—	,,	0·0037	0·0015	,,	0·0005	0·0047	0·0008
79	12–14% Cr (annealed and cleaned)	0·1	—	—	12/14	0·4	—	—	—	,,	nil	0·0002	,,	nil	0·0026	0·0002
24	15–18% Cr	0·07	0·24	0·24	15/16	—	—	—	—	,,	0·0031	0·0014	,,	0·0007	0·0034	0·0005
29	15–18% Cr	<0·12	<0·5	0·2/0·4	16/18	<0·1	—	—	—	0·0001	0·0039	0·0015	0·0003	0·0036	0·0025	0·0005
93	15–18% Cr	<0·12	<1·2	<0·5	15/18	<0·25	—	—	—	nil	0·0051	0·0009	nil	0·0013	0·0034	0·0005
170	15–18% Cr	0·11	0·33	0·36	17·45	—	—	—	—	—	—	0·0033	—	0·0003	0·0065	0·0005
177	15–18% Cr	1·05	—	0·45	17·5	0·35	—	—	—	—	—	0·0074	—	0·0002	0·0015	nil
108A	15–18% Cr	1·20	0·5/1·0	—	17	—	—	—	—	—	0·0053	0·0021	0·0005	0·0021	—	0·0012
							Nickel–Chromium Steels (Increasing Ni content).									
					12/14	1·0/1·5	—	—	—	nil	0·0030	0·0029	0·0002	0·0027	0·0040	0·0003

	Nickel–Chromium Steels (Increasing Ni content).																
28	12–14 Cr + Ni	0·15/0·2	<0·5	0·2/0·4	12/14	1·0/1·5	—	—	—	nil	0·0030	0·0029	0·0002	0·0027	0·0040	0·0003
31	12–14 Cr + Ni (ann'd, pickled and oil quenched)	0·10/0·18	—	—	13·26	2·1	—	—	—	,,	0·0041	0·0011	nil	0·0014	0·0035	0·0002
16	18/8 Cr Ni	0·10	—	—	18·0	9·5	—	—	—	,,	nil	0·0001	,,	nil	0·0022	0·0001
27	18/8 Cr Ni	<0·25	<0·5	0·2/0·4	17/19	7/9	—	—	—	,,	0·0080	nil	0·0002	0·0258	0·0013	0·0042
55	18/8 Cr Ni (annealed, pickled and quenched)	0·08/0·16	—	—	15·55	11·18	—	—	—	,,	nil	0·0001	nil	nil	0·0036	0·0002
57	18/8 (heat treated, pickled)	<0·15	0·3/0·6	0·3/0·6	17/20	7/10	—	—	—	,,	,,	0·0003	,,	0·0004	0·0028	0·0001
69	18/8 ,, ,,	<0·2	0·4/0·7	0·35/0·5	17·8/18·8	7·75/9·0	—	—	—	,,	0·0006	0·0002	0·0001	0·0005	0·0010	0·0002
77	18/8 ,, ,,	<0·15	<0·5	<0·5	17/19	8·5/9·5	—	—	—	,,	nil	0·0001	nil	nil	0·0076	nil
136	18/8 ,, ,,	Low	—	—	18	8	—	—	—	,,	,,	nil	,,	,,	0·0023	0·0002
154	High Cr–Ni alloy	0·12	—	—	23·75	9·11	—	—	—	,,	—	,,	,,	,,	0·0009	0·0001
95	High Cr–Ni alloy	—	—	—	21/24	13	—	—	—	,,	0·0002	0·0002	0·0001	0·0018	0·0034	0·0002
156	High Cr–Ni alloy	0·11	—	—	26·26	15·93	—	—	—	,,	nil	nil	nil	nil	0·0006	nil
157	High Cr–Ni alloy	0·059	—	—	27	10·73	—	—	—	,,	—	,,	,,	,,	0·0010	0·0001
26	8/18 Cr–Ni	0·3/0·4	<0·5	0·2/0·4	8/10	17/19	—	—	—	0·0002	0·0013	0·0001	0·0017	0·0081	0·0026	0·0011
67	8/18 Cr–Ni	0·42/0·48	0·8/1·4	0·5/0·7	6·75/7·75	18·8/19·9	—	—	—	nil	0·0100	0·0019	0·0001	0·0311	0·0025	0·0021
68	8/18 Cr–Ni	0·1/0·2	1·0/1·4	0·5/0·7	6·75/7·75	18·8/19·5	—	—	—	,,	0·0033	0·0017	0·0001	0·0118	0·0023	0·0007
32	High Cr–Ni alloy	0·15/0·25	0·75/1·5	0·5/0·7	24/26	19/21	—	—	—	,,	nil	0·0001	nil	nil	0·0008	nil
60	High Cr–Ni alloy	0·1	0·83	0·72	31·72	20·0	—	—	—	,,	,,	0·0001	,,	,,	0·0011	,,
59	High Cr–Ni alloy	0·13	0·77	0·73	19	32	—	—	—	,,	0·0031	0·0015	,,	0·0001	0·0029	0·0002
147	High Cr–Ni alloy (hot rolled)	—	0·3	2·5	22	32	—	43	—	,,	0·0007	0·0013	0·0001	0·0004	0·0029	0·0007
149	High Cr–Ni alloy (cast)	—	2·0	2·5	20	32	—	43·5	—	,,	0·0024	0·0010	nil	0·0010	0·0022	0·0395
111	High Cr–Ni alloy (cast)	—	—	—	16/19	35/38	—	—	—	,,	0·0033	0·0023	,,	nil	0·0029	0·0005
148	High Ni–Cr alloy	—	—	2	16	59	—	23	—	,,	—	nil	0·0001	0·0030	0·0015	0·0007
107	High Ni–Cr alloy	—	—	2	19·5	77·5	—	1 max.	—	,,	0·0022	0·0019	0·0001	0·0021	0·0021	0·0007
	Molybdenum Steels.																
58	18/8+Mo	0·15	0·3/0·6	0·3/0·6	17/20	7/10	2·25 / 2·75	—	—	,,	nil	0·0001	nil	nil	0·0022	0·0001
99	Cr–Ni–Mo–W alloy	—	—	—	14	58	17	6	5	—	—	nil	—	,,	nil	—
100	Ni–Mo alloy	—	—	—	—	60	20	20	—	,,	0·0029	,,	0·0001	0·0015	0·0061	0·0018
	Tungsten Steel.																
63	High Cr–Ni–W alloy	0·25	1·52	0·43	11·44	58·6	—	3·2	—	,,	0·0008	0·0006	nil	0·0001	0·0014	0·0006
	Silicon Steels.																
						Fe.											
93	17% Cr	<0·12	<1·2	<0·5	15/18	<0·25	—	—	—	nil	0·0055	0·0009	,,	0·0013	0·0034	0·0003
149	High Cr–Ni (cast)	—	2·0	2·5	20	32	43·5	—	—	,,	0·0024	0·0010	,,	0·0010	0·0022	0·0395
103	Cr–Ni–Si	0·25	5	—	12	35	—	—	—	,,	0·0028	0·0011	,,	0·0007	0·0021	0·0002
	Copper Steels.																
									Cu.								
74	Cu steel	0·07	0·008	0·45	—	—	—	—	0·24	0·0027	0·0055	0·0046	0·0018	0·0225	0·0036	0·0124
73	Cu steel	0·04	0·005	0·13	—	—	—	—	0·264	0·0041	0·0072	0·0048	0·0021	0·0030	0·0044	0·0097
72	Cu steel	0·07	0·009	0·35	—	—	—	—	0·318	0·0033	0·0048	0·0045	0·0020	0·0124	0·0053	0·0135
61	18/8+Cu	0·48	1·0	0·97	8·26	21·9	—	—	1·02	nil	0·0032	0·0024	nil	0·0167	0·0027	0·0011
56	High Cr–Ni + Cu	0·3/0·5	1·25/1·5	0·6/0·9	7·5/9·0	21·5/23·5	—	—	1·0/1·5	,,	0·0029	0·0023	,,	0·0315	0·0031	0·0037
76	20% Cr + Cu	0·3	—	—	20	—	—	—	1	,,	nil	0·0001	,,	0·0003	0·0028	0·0001
117	Alloy C.I.	2·8/3·0	2·0/2·5	1·0/1·2	1·3/4·0	12/15	—	—	5·0/7·0	0·0001	0·0030	0·0036	0·0001	0·0145	0·0022	0·0030
178	Alloy C.I.	3·10	1·88	0·78	2·57	13·46	—	—	6·26	—	—	0·0029	—	0·0130	0·0008	nil

These curves are the average of a number of results. The values varied in some cases by as much as 100 per cent, but the trend of the corrosion is so marked that they can be taken to confirm the deductions already drawn from laboratory experiments.

In Fig. 10 the effect of the type of corrosive material on the necessary composition of the resisting steel is clear. For example a 5 per cent Cr steel reduces the corrosion rate in the vapour-phase section of evaporators to 8 per cent whereas even 14 per cent Cr is not sufficient for this reduction in the liquid-phase section of cracking tubes. The shape of the curves is also of interest, economics suggesting that additional Cr beyond 14 per cent may not give corresponding increases in life except in the presence of H_2S, where over 20 per cent Cr is indicated by extrapolation.

Experiments have been carried out at the authors' works in an atmosphere of steam with 4 per cent added H_2S, at a temperature of 185° C and 4·7 atm pressure, and although only few types of steel were used, the results as shown in Fig. 11 again indicate the advantage of an increase in chromium content. A notable point in this series, which is brought out in later curves, is the deleterious effect of additions of nickel under certain conditions with a sulphur-containing atmosphere, the two highest chromium steels being somewhat worse than those with a lower chromium content, presumably due to the high nickel content. The effect on the results of the particular conditions prevailing in service is clearly shown in the big discrepancy between the results of preliminary tests (curve A) and those carried out later (curve B), under approximately similar conditions when it was considered that the alteration was due to obtaining drier conditions of test.

Scaling.

Corrosion at temperatures higher than 250° C can be considered under the heading of scaling as previously mentioned. Tests have been carried out in the Research Department of the authors' firm at various temperatures up to 1050° C in various controlled atmospheres, and although these high temperatures may not be particularly applicable to the petroleum industry, the general trend of the results may be some guide to the resolving of difficulties which arise in such plants.

The results of scaling tests are sometimes anomalous because of the method of attack. This is usually to form a thin layer of oxide, which grows and gives rise to an apparent increase in weight of the specimens until a certain limit is reached when the scale tends to flake off, and the process is repeated. Scaling proceeds therefore in a series of steps, and a true test must take into account sufficient of these to even out irregularities due to tests being taken before or after the scale has flaked. In the tests to be discussed, a period of 3000 hours has been taken as the standard. Shorter periods than this are considered only where the results are so definite that further exposure was obviously unnecessary.

The test pieces were cylindrical in shape, 1 in dia × 1 in long. Each series of specimens was heated in a tubular electric furnace, being supported on heat-resisting steel skids, in order to ensure uniform heating, freedom from reaction with the refractory, and ease of removal.

Any possible effect of position in the series on the scaling conditions was

overcome by moving the specimens progressively after each weighing so that each in turn occupied every position on the skids.

Scaling Tests at Temperatures up to 750° C. Fig. 12 gives the results of tests carried out in an atmosphere of burnt town's gas (CO_2 4·5 to 5·0; O_2 12·5 to 13·0; CO nil; N_2 (diff) 82 to 83 per cent) at temperatures of 450° to 550° C. There is a pronounced effect of an increase in chromium content, and it is clear that at this temperature increases of chromium much beyond 5 per cent are hardly justifiable as the rate of scaling even of mild steel is quite low. The results of tests carried out at 650° and 750° C in a similar atmosphere and also with the addition of SO_2 to the atmosphere are shown

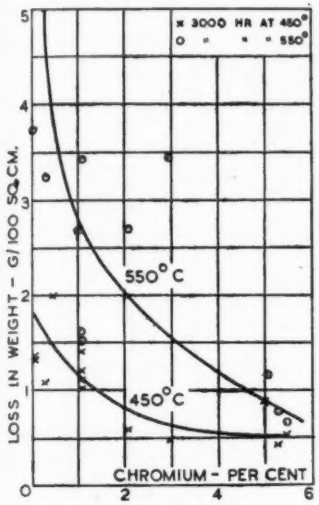

FIG. 12.

EFFECT OF CHROMIUM ON SCALING IN BURNT TOWN'S GAS. (3000 HR AT 450° C AND 550° C.) (CYLINDRICAL TEST PIECES, 1 INCH DIA × 1 INCH LONG.)

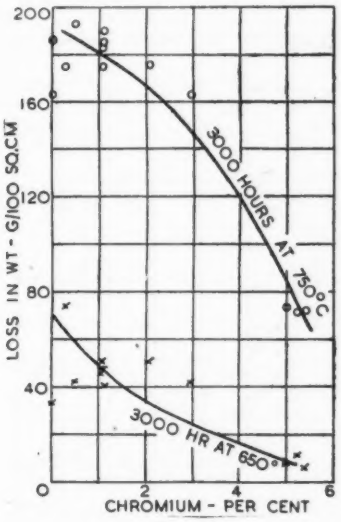

FIG. 13.

EFFECT OF CHROMIUM ON SCALING IN BURNT TOWN'S GAS. (3000 HR AT 650° C AND 750° C.) (CYLINDRICAL TEST PIECES, 1 INCH DIA × 1 INCH LONG.)

in Figs. 13 and 14. Although the tests are carried out on steels containing only up to 5 per cent chromium, the beneficial effect of increasing percentages of this element is becoming very apparent. The effect of SO_2 on the tests at 650° C is very marked, increasing the scaling by up to 30 per cent, whereas at 750° C the effect is negligible. This apparently anomalous effect at 750° C is in line with results obtained at higher temperatures as shown later.

Scaling Tests at 950° C. Fig. 15 gives the results of tests carried out at the higher temperature of 950° C. Low alloy contents are of little value in preventing scaling at these temperatures, and the minimum chromium content in this series is 13 per cent. Many of these steels contained high percentages of nickel, so that the effect of the chromium is masked to some

extent. The scatter of the points in this figure and in the three subsequent ones portrayed is due to the fact that no one factor can be isolated from another as the main cause of a particular scaling effect. Thus, not only chromium and nickel are of significance, but the secondary elements also, a number of which may be present in any one alloy. Again factors relating to methods of fabrication and heat treatment cannot be excluded as influencing the rate of scaling. Nevertheless in Fig. 15 the effect of increases in chromium beyond 20 per cent are quite clear, and the dotted lines indicate the general situation of the points. The additive effects

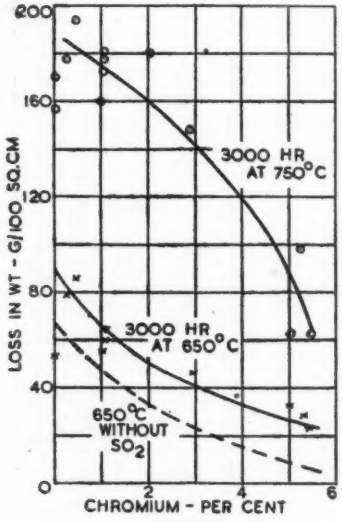

FIG. 14.

EFFECT OF CHROMIUM ON SCALING IN BURNT TOWN'S GAS, CONTAINING 0·043 PER CENT ADDED SO_2. (3000 HR AT 650° C AND 750° C.) (CYLINDRICAL TEST PIECES, 1 INCH DIA × 1 INCH LONG.)

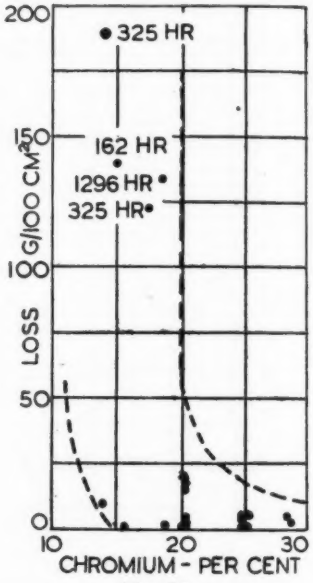

FIG. 15.

EFFECT OF CHROMIUM ON SCALING IN BURNT TOWN'S GAS. (3000 HR AT 950° C.) (TEST PIECES 1 INCH DIA × 1 INCH LONG.)

of the chromium and nickel are shown in Fig. 16 in which the sum of the contents of these elements is compared with the loss by scaling. There is still a considerable scatter, but most of the apparent anomalies have been corrected and the band indicated by the lines emphasises the value for scale resistance of the more highly alloyed compositions.

The effect of additions of SO_2 to the atmosphere are found to depend largely upon the type of atmosphere which is present. In Fig. 17 the results of the addition of SO_2 to an atmosphere of burnt town's gas illustrates this point. The dotted lines defining the central band are taken from Fig. 15 and show the nature of the scatter of points in a town's gas-fired furnace.

The effect of additions of SO_2 with an oxidizing atmosphere, shown by the dots in Fig. 17, is, in general, to reduce the rate of scaling. When the

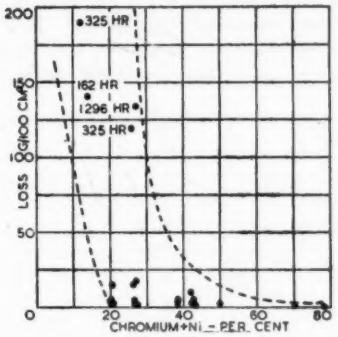

FIG. 16.

EFFECT OF ADDITIONS OF CHROMIUM AND NICKEL ON SCALING IN BURNT TOWN'S GAS. (3000 HR AT 950° C.) (TEST PIECES 1 INCH DIA × 1 INCH LONG.)

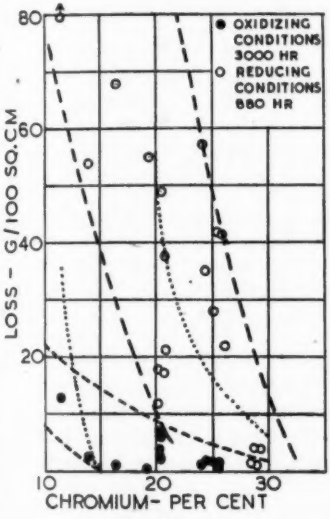

FIG. 17.

EFFECT OF CHROMIUM ON SCALING OF STEELS AT 950° C IN BURNT TOWN'S GAS WITH 0·043 PER CENT ADDED SO_2, UNDER (*a*) OXIDIZING CORRODING CONDITIONS, AND (*b*) REDUCING CONDITIONS. (TEST PIECES 1 INCH DIA × 1 INCH LONG.)

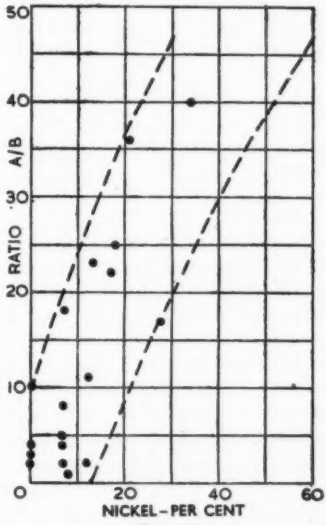

FIG. 18.

EFFECT OF NICKEL ON RELATIONS BETWEEN SCALING IN (*a*) OXIDIZING AND (*b*) REDUCING BURNT TOWN'S GAS ATMOSPHERES CONTAINING 0·043 PER CENT SO_2 AT 950° C.

atmosphere is changed to a reducing one the scaling increases enormously; the circles in Fig. 17 show this effect and are for a period of only 880 hours,

compared with 3000 for the oxidizing conditions. In all cases the beneficial effect of additions of chromium is still evident.

An explanation of the increase in scatter of the points in Fig. 17 is obtained when the nickel content is considered. In Fig. 18 this is plotted against the proportionate increase in scaling loss when changing from an oxidizing atmosphere with SO_2 (3000 hours) to a reducing atmosphere with

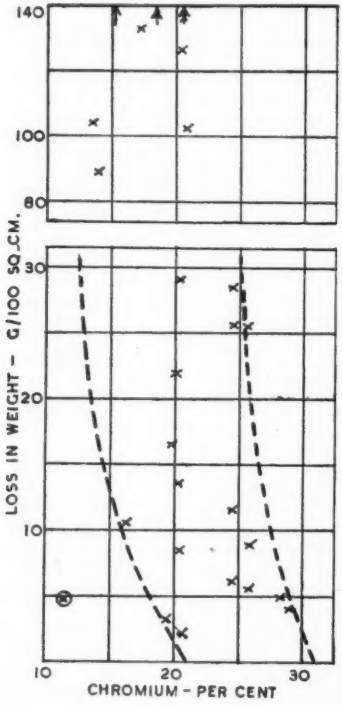

FIG. 19.

EFFECT OF CHROMIUM ON SCALING IN BURNT TOWN'S GAS. (3000 HR AT 1050° C.)
Note: the deviation of the ringed point from the rest is due to the presence of aluminium.

SO_2 (880 hours). It is clear that as the nickel content increases, the resistance to scaling by SO_2 in a reducing atmosphere is decreased to a very considerable extent.

The importance therefore of knowing the exact conditions under which scaling resistance is required is emphasized by a comparison of Figs. 16 and 18. In the former figure, the increases of nickel show an additive beneficial effect, whereas in the latter they exhibit a pronounced deleterious result.

Scaling Tests at 1050° *C.* The results of tests carried out at 1050° C in an atmosphere of burnt town's gas are shown in Fig. 19. The relation

between scaling and chromium content is again evident, the safest range for resistance being increased to 25 per cent chromium and upwards, with the 30 per cent chromium steels being easily the best; the low scaling results of three alloys with approximately 12 and 20 per cent chromium are due to large increases in other elements, such as aluminium, which are not considered in detail in this paper.

Properties at High Temperatures.

When a steel is used at a high temperature its strength becomes reduced and even the definition of strength has to be adjusted because of the altered conditions. At room temperature the strength of a test piece, as determined in the usual manner by means of a tensile machine, has a fixed value which is virtually independent of the method of applying the tensile stress, but as the temperature is increased the method of application becomes an important factor in the result. If the stress is applied slowly, it is found that the test piece will stretch appreciably at stresses which are much below those which are obtained by a quick pull. This property is known as "creep," and is important in the design of structures which have to withstand stresses at high temperatures. Various standards are used to indicate the creep of the steel, but in the results which follow the basis taken is that the creep strength at a given temperature is the stress which will produce a rate of creep of 10^{-6} in/in/hr when measured after 1000 hours under conditions of constant temperature and stress.

For the present purpose it is convenient to study the steels under three heads corresponding roughly to the divisions already made in the discussion of corrosion, *i.e.*, low alloy steels, medium chromium steels, and higher alloy steels of the austenitic type.

Low Alloy Steels.

These steels have reasonable strength at temperatures up to 550° C. The creep strength of a selection of these and their mechanical properties as derived by a quick-pull tensile test in this range of temperature are shown in Table III, which also indicates the usual type of operation for which they are used.

The addition to the mild steel of a small amount of molybdenum, steel *a*, produces an increase in the creep strength of about 100 per cent, and other mechanical properties remain very high throughout the range. A further increase in the molybdenum content gives a further increase in the creep strength and an increase also in the other properties.

To give increased tensile strength at normal temperatures for steel used for bolts, the carbon content is increased as in steels *c* and *d*. In steel *c* the creep strength still remains high, whereas in steel *d* the increase in the cold strength is accompanied by a slight loss in the creep strength, though again this is balanced by an increase in the resistance to corrosion and scaling by the addition of the 1 per cent Cr. This latter steel is very widely used for bolts as it is also free from embrittlement due to long-time operation at elevated temperatures. As an indication of further uses, this steel is being employed for jet-propulsion engine discs.

The last in this series is the modified 4 to 6 per cent Cr steel, which is used because of the increased corrosion resistance although the other

TABLE III.

Ferritic Steels used in Petroleum Industry. Mechanical Properties and Creep up to 550° C.

Type.	Treatment.	Typical analysis.					Test temp, °C.	Mechanical properties.						Creep * strength, (tons/sq. in).	Use.
		C.	Si.	Mn.	Cr.	Mo.		L.P. (tons/sq. in).	Y.P. (tons/sq. in).	M.S. (tons/sq. in).	El %.	R.A. %.	Izod.		
Mild steel		0·10/0·15	—	—	—	—	15	15·4	18·7	27·9	36·0	67·5	80	—	—
							450	5·4		22·5	35·5	68·4		7·5	
							500	4·7		19·0	40·0	73·2		4·0	
							550	3·5		15·7	43·2	77·5		1·5	
(*a*) Low C Low Mo	Annealed	0·12	0·3	0·4	—	0·3	15	12·0	14·5	25·5	40·0	67·4	43	—	Superheater tubes.
							400	8·0		28·0	43·0	76·0		—	
							450	6·8		23·5	41·5	75·4		13·0	
							500	6·1		20·0	38·4	74·0		7·5	
							550	—		—	—	—		3·0	
(*b*) Low C High Mo	Normalized	0·12	0·3	0·4	0·3	0·8	15	18·0	23·8	33·2	34·5	65·8	87	—	Superheater tubes.
							400	10·0		40·1	28·0	67·0		—	
							450	8·5		35·7	26·0	65·4		22·0	
							500	7·7		2·5	23·0	66·0		15·0	
							550	—		—	—	—		8·0	
(*c*) High C High Mo	Quenched and Tempered	0·25	0·3	0·4	0·3	0·8	15	46·0	46·5	54·0	24·0	63·7	88	—	Flange bolts, etc.
							400	26·8		47·8	29·2	66·1		—	
							450	23·2		43·9	22·3	68·5		24·5	
							500	21·0		39·2	23·1	69·1		15·0	
							550	17·5		36·5	23·8	74·5		5·0	
(*d*) 1% Cr, Mo	Quenched and Tempered	0·35	0·35	0·5	1·0	0·7	15	59·0	59·8	67·0	22·0	63·7	85	—	Flange bolts, etc.
							400	32·5		55·0	20·7	62·3		—	
							450	30·8		50·0	24·0	71·5		23·5	
							500	29·5		44·0	27·0	77·0		11·5	
							550	27·8		38·0	28·5	84·0		3·0	
(*e*) 5% Cr, Mo	Annealed	0·15	0·5	0·5	5·0	0·5	15	12·0	16·0	35·8	35·5	67·8	107	—	Still tubes and fittings.
							400	9·0		30·0	27·0	60·0		—	
							450	8·2		27·0	28·4	63·6		12·5	
							500	7·0		25·2	32·5	67·2		7·0	
							550	—		—	—	—		5·0	

* Stress required to give rate of creep of 10^{-6}/hr at 1000 hrs.

high-temperature properties are somewhat lower than those already considered.

The ductility of steels *a*, *b*, and *e* is high, and they can be easily drawn into tubes for superheaters and stills. Steels *c* and *d* are for high-tensile work, and naturally have a lower ductility.

Medium Chromium Steels.

This type of steel is illustrated in Table IV. This steel is the simple stainless type, and is employed chiefly for its corrosion-resisting properties.

TABLE IV.

13% Cr *Types.*

Tests at Normal Temperatures.

Type.	Treatment.	Y.P. (tons/sq. in).	M.S. (tons/sq. in).	El (%).	R.A. (%).	Izod.
Low C, 13% Cr	Oil quenched and tempered	30·8	43·2	30·0	70·0	95
0·25% C, 13% Cr		39·0	51·0	26·0	51·0	43
Low C, 13% Cr, Mo, V		35·0	48·8	27·0	64·0	95

Creep Strength.

Type.	Creep strength (tons/sq. in).		
	450°.	500°.	550°.
Low C, 13% Cr	10·7	6·8	3·4
High C, 13% Cr	9·4	4·9	2·3
Low C, 13% Cr, Mo, V	18·0	9·2	4·4

The usual type of stainless steel is shown in the first line in which the normal strength and the creep strength are given. To increase the strength at normal temperatures the carbon content can be raised as in the second line, but there is a resultant drop in the impact value and in the creep resistance. With the addition of both Mo and V, however, a steel can be obtained in which the initial strength is equal to that of the high-carbon steel, the impact value is restored to that of the low-carbon type and the creep resistance is not only restored but increased.

Austenitic Steels.

The basic steel of this type is the 18 per cent chromium–8 per cent nickel composition, and this is used as the standard for comparison in Table V which gives the properties of these steels.

The plain 18/8 is susceptible to corrosion embrittlement as discussed later, and this is overcome in an improved 18/8 containing Mo, W, and Ti. These additions also increase the high-temperature properties as shown in the second part of Table V, the creep values going up by at least 50 per cent.

The increase of the Cr and Ni to 20/10 will, as explained previously, increase the corrosion and scaling resistance. The steel next in the list in

* Stress required to give rate of creep of 10^{-4}/hr at 1000 hrs.

Table V is such a steel with the addition of W, and the creep resistance is definitely superior to that of the improved 18/8. This steel can be used in situations in which a considerable strength even at temperatures of the order of 950° C is required.

A further increase in the Cr and Ni contents will raise the corrosion resistance except in the case of sulphurous atmospheres, and the strength of the standard 25/18 steel shown next in Table V is still considerable at the elevated temperature, although not as high as that of the alloy previously considered.

TABLE V.

Austenitic Steels.

Tensile Strength at Normal and Elevated Temperatures.

Type.	Test temp. (° C).	Y.P. (tons/sq. in).	M.S. (tons/sq. in).	El (%).	R.A. (%).	Izod.
18/8	15	15·0	41·0	70	75	100
18/8 + Mo, W, Ti	15	28·0	52·5	46	53	93
20/10 + W	15	38·0	61·0	34	40	35
	700		31·0	35	57	
	800		24·6	36	60	
	900		17·7	43	64	
25/18	15	24·0	43·0	45	55	50
	700		28·0	33	50	
	800		20·0	33	48	
	900		15·0	31	48	
14/14 + W	15	26·0	52·5	32	45	75
	700		29·8	29	48	
	800		22·0	37	62	
	900		17·2	39	65	

Creep Strength.

Type.	Creep strength (tons/sq. in).						
	500.	550.	600.	650.	700.	750.	800.
18/8 . .	—	7¼	4¼	3	2¼	—	—
18/8 + Mo, W, Ti	17	12¼	8	5½	3½	—	—
20/10 + W .	—	—	8½	6½	4½	2¾	1½
25/18 . .	—	—	5	3½	2	1	¾
14/14 + W .	—	—	7	4	2½	1¼	¾

Another steel of this series is the 14/14 composition and is given in Table V. The high-temperature properties are still very good. This steel shows no embrittlement and is extensively used in such exacting conditions as the exhaust valves of internal-combustion engines.

In general it may be said of the steels considered in this section, that, by suitable modification of the plain composition, whether mild steel or the corrosion-resisting higher alloyed steels, by the addition of small amounts

of other elements such as Mo, W, V, and Ti the original properties can be retained and high-temperature strength also imparted.

The Fabrication of the Steel.

The steel is usually tapped from the melting furnace into a ladle and from this poured either into ingots or into sand moulds. In the case of the ingots, these are subsequently treated by forging, rolling, pressing, or drawing to put the steel into shape suitable for the purpose required. In the case of the castings, these are made to approximately the final required shape. With either method the final product may be either a complete article or a part of an article, the various sections being later riveted, bolted, or welded together.

Most of the steels which have been discussed here occasion no great difficulty in fabrication. The casting temperature has usually to be controlled within fairly narrow limits so as to avoid undesirable features either in the ingot or the casting, and the forging or other hot-working has also to be accurately controlled. In the case of steels which are of high creep strength, it is clear that these require high temperatures before they can be made sufficiently ductile to forge easily and at the same time the melting point is also lowered by the alloy additions thus reducing the temperature range within which hot working can be safely carried out. In addition to the general precautions which have to be taken, there is need for special care in the handling of certain of the steels because of their own inherent properties. The majority of these troubles in fabrication lie within the field of the manufacturer and, as such, are of little interest to the customer if he has obtained his material from a manufacturer who possesses the necessary facilities for a close control of his processing. Certain types of fabrication, however, such as welding, are carried out by the user on site, and for this reason it is desirable that he should know the particular technique which is needed in dealing with the material with which he is working. For this reason the unusual details of the working and welding of each steel have been included in the later section, in which each of the different types has been dealt with individually.

However, in view of the rapid strides which have been made in recent years in the production of intricate designs by means of castings, it is desirable to deal rather more fully at this stage with this method of fabrication.

Development of Castings.

Prior to the last war, castings were regarded as one of the poorer forms of metal structures. Forgings were considered to be much superior, being regarded as completely sound, whereas castings were held to be largely subject to internal defects such as blow holes or shrinkage cavities. With the development of radiography of castings, largely occasioned by the need for a greatly improved and increased output during the war for castings for aircraft, the standard has undoubtedly been enormously improved. X-ray equipment, installed as an essential requirement for the production of aircraft parts, has been used for the development of other forms of castings. Although the method has been mainly applied to light-alloy castings, it has

also proved of great benefit for steel and heavy metal castings. Strangely enough, in the works with which the authors have been connected, one of the earliest types of castings to be examined for defects was for the petroleum industry, and the type of casting is shown in Fig. 20. These header castings were suspected of being unsound and were radiographed, when the unsoundness was revealed. The extent of the trouble is shown in Fig. 21, which shows part of one of these castings after sectioning. An alteration in the method of manufacture enabled this trouble to be eliminated. A study of other types of castings which have been made and improved by the use of radiography has been published by one of the authors (R.J.),[16] and a few examples taken from this source will illustrate the value in service of castings which have been proved to be sound by radiography. A high-temperature high-speed fan, consisting of a number of special alloy blades, as shown in Fig. 22, attached to a rotor, had previously given trouble because the separate blades during final grinding to shape were found to contain extensive sub-surface defects. The manufacture was put under radiographic control and experiments made to determine the most satisfactory method of casting.

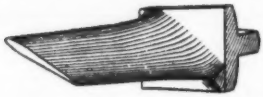

FIG. 22.

HIGH-TEMPERATURE, HIGH-SPEED BLADE MADE AS A CASTING.

It was found that a visually perfect casting might contain two types of defects. These, illustrated by sections of defective castings, are shown in Figs. 23 and 24. The former is clearly a weakness in the blade, whilst the second would give rise to the grinding troubles previously experienced. After preliminary trials and examinations, the causes of both these types of defect were found and eliminated. The product was then made entirely successfully as confirmed by occasional check radiographic examinations during production.

Another type of casting consisting of a box built up of a number of flat plates and used under high-temperature, highly corroding conditions had been found to fail in service, the breakdown being revealed under investigation to be due to internal unsoundness. Research into methods of improving the quality of the $\frac{5}{16}$ in thick plates resulted in a considerable reduction in the amount and severity of the unsoundness. Fig. 25 shows a radiograph of one of these plates with sections taken from the plate to reveal the extent of the defects. Three plates, two showing early stages in the investigation and the third the method finally adopted, are illustrated diagrammatically in Figs. 26, 27, and 28. The SH number in the figures represents the severity of the shrinkage defects in the area on a scale of severity increasing from 0 to 10; in addition, the hatching indicates medium-size defects and the cross hatching, severe defects. The areas marked " head " in Fig. 28 are not, of course, defects, but are sound metal and indicate the position of the feeding heads. The final method results in a degree of soundness which is as high as can probably be obtained in this thickness of plate with the particular steel necessary for corrosion resistance.

A valuable use of radiography is in the examination of highly stressed castings to ensure that no defects of a dangerous size are present. During the war two very difficult steel castings were made for aircraft; the first, a pivot bracket, shown in Fig. 29, was a part of the undercarriage for the Hawker Typhoon, and was an extremely difficult casting to make. Any failure of this casting would lead to destruction of the plane and loss of life, so the highest possible soundness was required. Each of these castings was radiographed in the vital places, and as far as is known, out of several thousands put into operation, not one failed in service. The eye shown in

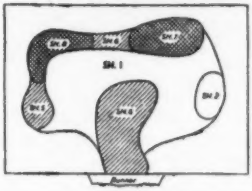

FIG. 26.

DIAGRAMMATIC SKETCH OF PLATE SHOWING DEFECTS IN EARLY METHOD OF MANUFACTURE. SH NOS. REFER TO SEVERITY OF SHRINKAGE DEFECTS ON A SCALE INCREASING FROM 0 TO 10. MEDIUM-SIZE DEFECTS SHOWN BY HATCHING, SEVERE DEFECTS BY CROSS HATCHING.

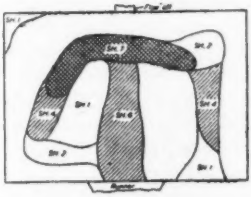

FIG. 27.

DIAGRAMMATIC SKETCH OF PLATE SHOWING DEFECTS IN EARLY METHOD OF MANUFACTURE.

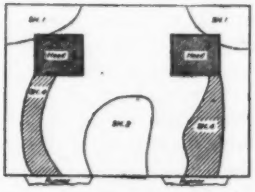

FIG. 28.

DIAGRAMMATIC SKETCH OF PLATE SHOWING RESULTS OF FINAL METHOD OF CASTING.

the front of the photograph, although containing a thickness of only 0·25 in CL of steel, was subjected to considerable tensile stress. To determine the standard to be adopted in the X-ray inspection of these castings, six of the brackets which had been rejected by radiography for defects in the vicinity of this eye were tested to destruction. The maximum working load was estimated at 16·6 tons, but with safety factors this value was increased to a required maximum test load of 39·5 tons. The results of the tests on these six brackets taken in pairs are given in Table VI. The first pair failed due to shearing of the bolts holding the brackets to the test bed. These bolts were increased in strength by substituting high-tensile steel for mild steel and were increased in cross-section by 50 per cent, but the second test again failed due to stripping of the nuts. With these, also made of high-tensile steel, a third test successfully took the casting to destruction. The load imposed on these three pairs of castings known to be defective show that even in these cases a safety factor of more than 2·5 was obtained.

TABLE VI.

Results of Tests to Destruction on Pivot-Bracket Castings.

Estimated maximum working load—16·6 tons.

Castings. examined.	Max. load attained (tons).	Results.	Conclusions.
First pair.	37·4	Holding-bolts sheared.	Breaking-load not reached.
Second pair.	46·8	One casting cracked, nuts stripped and holding-bolts sheared.	One casting cracked.
Third pair	42·3	One casting broke.	One casting failed.

As this safety factor is incorporated in the design, largely to allow for internal unsoundness, it would presumably be possible to redesign the castings and lighten them so that a satisfactory breaking load, but one much less in excess of the maximum required, could still be obtained. Another high-tensile casting for the Tempest aircraft, the rear spar-bay casting, is shown in Fig. 30. This part was originally built up from 64 separate forgings. The technique for this casting was also developed by means of radiography, and of the thousands of castings afterwards tested by a proof load, not one failed in its test. The load imposed in this proof test, which presumably included sufficient allowance for safety factors, was 69·9 tons, in tension in the top two lugs and in compression in the bottom two. A casting selected at random was stressed to destruction, and one of the top eyes eventually opened out at a load of 140 tons. Here again, the actual strength of the casting is much in excess of that required.

Further work on castings for high-temperature high pressure pipelines has been reported by Keating.[17] In this situation radiographically examined castings are apparently giving good service.

Although the majority of the samples quoted have not been for castings suitable for the petroleum industry, the techniques of manufacture which have been developed on these special designs can be applied to other types of castings, and there is no doubt that, for shapes of an intricate nature, castings offer a great advantage over other forms of fabrication. As shown by the above examples, they can under proper control give results which are comparable and possibly even superior to those obtained by other methods.

CHARACTERISTICS OF TYPICAL STEELS FOR SPECIAL PURPOSES.

In the previous sections a study has been made of the effects of alterations in the percentages of different elements upon certain properties of the steels, and it has become apparent that instead of a continuous range of steels for purposes in which service conditions vary from mild to very severe, it is possible to determine a number of compositions, each of which is reasonably satisfactory for a range of service conditions. For example, chromium steels can be divided into the low chromium, 5, 12, 20, and 30 per cent classes. Each of these has its own particular characteristics in addition to the special properties for which the steel is selected. As these character-

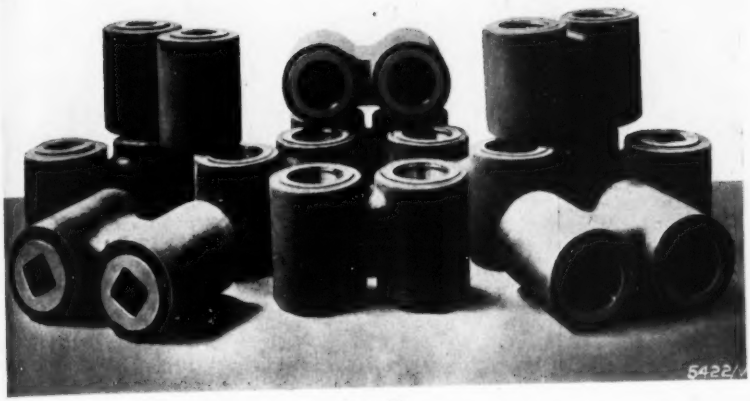

FIG. 20.

HEADER CASTINGS IN HEAT RESISTING STEEL. THIS TYPE OF CASTING WAS EXAMINED BY RADIOGRAPHY TO CHECK SOUNDNESS.

FIG. 21.

SECTION OF THE HEADER CASTING, BEFORE ALTERATION OF CASTING METHOD, SHOWING DEFECT REVEALED BY RADIOGRAPHY.

[*To face p.* 468.

FIG. 23.

SECTION OF DEFECTIVE FAN BLADE SHOWING SHRINKAGE CAVITY.

FIG. 24.

SECTION OF DEFECTIVE FAN BLADE SHOWING SUBCUTANEOUS PINHOLES.

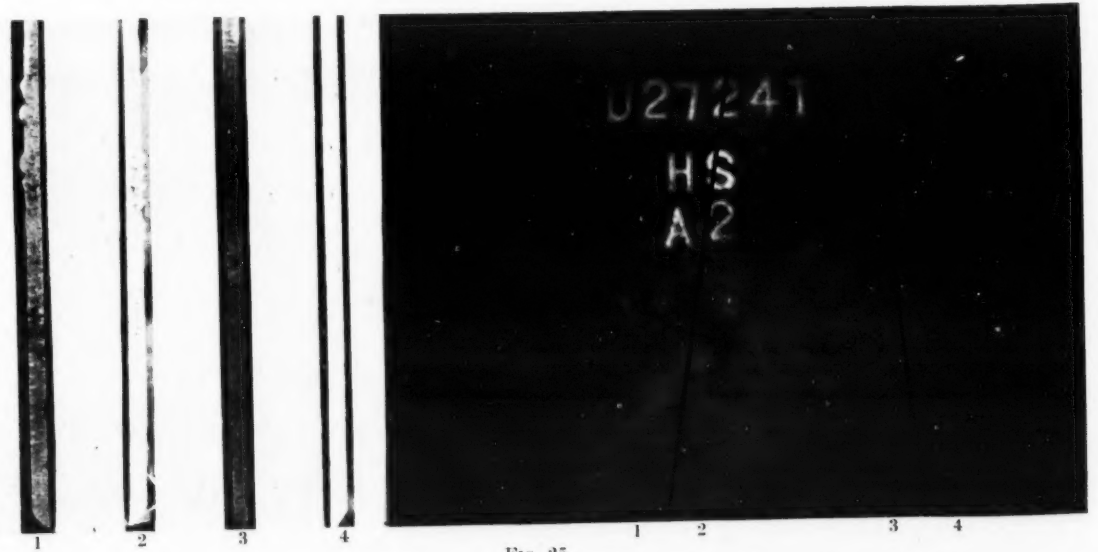

FIG. 25.

COMPARISON OF RADIOGRAPH OF PLATE SHOWING SEVERE THREADLIKE SHRINKAGE WITH PHOTOGRAPHS OF SECTIONS TAKEN IN PLACES INDICATED BY LINES ON RADIOGRAPH. SECTIONS 1 AND 3, AFTER POLISHING AND ETCHING, SECTIONS 2 AND 4, AFTER POLISHING ONLY. APPROX. BY $\frac{1}{3}$.

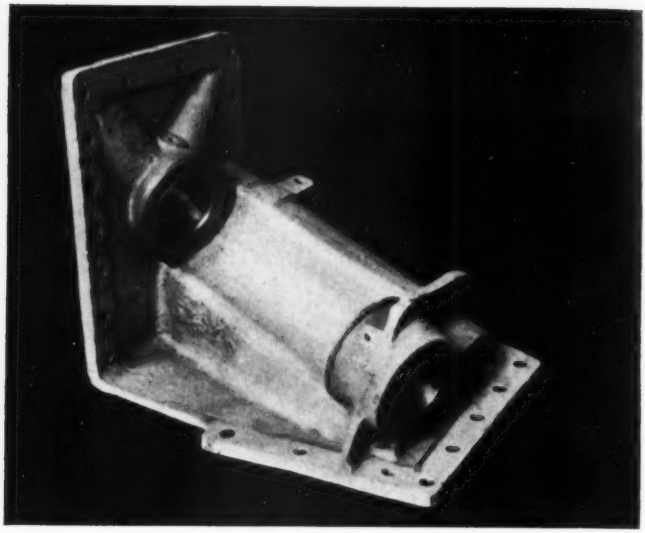

FIG. 29.

PIVOT-BRACKET CASTING FOR TYPHOON AIRCRAFT.

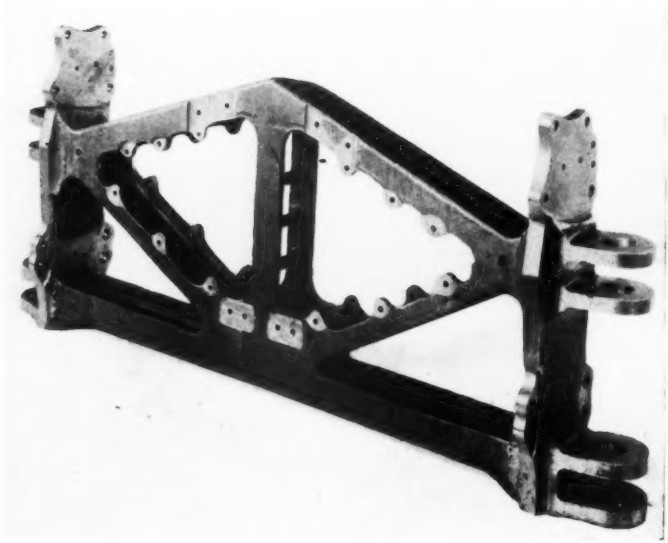

FIG. 30.

REAR SPAR-BAY CASTINGS FOR TEMPEST AIRCRAFT.

istics may determine the possibility of the use of the material in particular cases, some of the various types of steel are now considered in more detail.

4 to 6 per cent Chromium Steels.

These steels, which are relatively inexpensive, have a considerably improved resistance to corrosion compared with plain carbon steel, as shown in Fig. 10. That such steels also have a relatively high resistance to scaling and sulphur attack up to temperatures of the order of 600° C is apparent from the curves shown in Figs. 9, 10, 11, and 12. As a result, they have found wide application for such parts as cracking-furnace tubes, stills, hot-oil transfer lines, heat exchangers, return bends, flanges, etc.

The alloys have pronounced air-hardening characteristics, but can be softened by slow cooling from 850° C. This effect is illustrated in Table VII,[18] which shows the effect for three steels under three rates of

TABLE VII.

Air-Hardening Characteristics of 5 Per Cent Cr Steels.[18]

Effect of Rate of Cooling on the Mechanical Properties of 0·505 in Standard Bars.

C.	Cr.	Temperature of treatment, °C.	Cooling rate.	Tempering, °C.	Y.P. (tons/sq. in).	M.S. (tons/sq. in).	El, %.	R.A. %.	Brinell hardness.
0·10	5·20	870	In Air	None	48·3	80·0	15·5	53·2	361
0·20	5·20	855			50·7	94·0	9·0	18·5	417
0·30	5·30	855			52·5	98·5	13·5	31·7	448
0·10	5·20	870	In Air	600	45·5	50·8	20·0	71·0	250
0·20	5·20	855			53·4	61·2	18·5	58·7	272
0·30	5·30	855			52·0	61·1	18·0	60·5	275
0·10	5·20	870	Furnace Cooled	—	12·2	27·6	37·5	75·6	136
0·20	5·20	855			14·7	33·6	32·0	75·0	152
0·30	5·30	855			15·4	35·2	31·5	73·6	161

cooling. The air hardening effect can, however, be overcome by the addition of small amounts of titanium or columbium, as shown in Table VIII.[19] These elements combine with the carbon, which would

TABLE VIII.

Brinell Hardness of 5 Per Cent Chromium Molybdenum Steels after Air Cooling Showing Effect of Additions of Ti *and* Cb.[19]

	Standard steel.	0·39% Ti added.	0·50% Cb added.
Annealed . . .	137	149	146
Air cooled from 700° C .	137	146	146
„ „ 760° C .	134	149	146
„ „ 815° C .	311	149	146
„ „ 870° C .	363	146	146
„ „ 925° C .	363	149	156
„ „ 980° C .	375	143	217

otherwise be precipitated as chromium carbide and allow more chromium to remain in solid solution, thereby increasing the corrosion and scale resistance. An excess of the added element over that required for this purpose, however, promotes undesirable grain growth and a deterioration in properties.

In common with many other low alloy steels, these alloys are susceptible to temper brittleness, *i.e.*, brittleness brought about by slow cooling from the tempering temperature. This disability can be overcome by the addition of a small percentage of molybdenum. The effect of 0·5 per cent in this respect is illustrated in Table IX.[20] In this case the Mo addition

TABLE IX.

Effect of 0·50 *Per Cent* Mo *on* 4 *to* 6 *Per Cent* Cr *Steel, Annealed at* 840° *C.*[20]

Steel.	Treatment after anneal.	Izod value (average of 6).	Brinell hardness.	Susceptibility ratio.
A, 0% Mo	760° C temper, water cool.	96·5	137 to 143	1·000 (basis)
B, 0·50% Mo		101·0	143 to 149	1·000 (basis)
A, 0% Mo	760° C temper, air cool.	95·5	132 to 137	0·989
B, 0·50% Mo		101·5	143	1·005
A, 0% Mo	760° C temper, furnace cool.	53·0	137	0·555
B, 0·50% Mo		99·5	137 to 143	0·985

maintains the value of the impact test under conditions in which it would otherwise fall by about 50 per cent. The embrittlement in a straight 5 per cent Cr steel brought about by slow cooling becomes even more pronounced as a result of exposure for an extended period to a temperature in the range 400–550° C, and this indicates the advantage of the Mo-containing steels for service in which these temperatures are common.

The addition of molybdenum is also accompanied by an increase in creep strength, but although steels of the 4 to 6 per cent Cr–Mo type have creep properties much superior to plain carbon steels, they are inferior in this respect to other low-alloy steels, which are less resistant to corrosion and have been dealt with in the section of the paper concerned particularly with creep.

Fabrication.

Hot Working. The steels can be produced in the form of rolled or forged material in much the same way as an ordinary high-tensile steel. Owing to the air-hardening tendency previously referred to, however, they should be slowly cooled in a furnace or a suitable heat insulator such as sand or ashes, etc., after hot working, so as to avoid the danger of cracking. This precaution, as would be expected, however, is less necessary in the case of the Ti- or Cb-bearing steels.

Machining. Machining should follow the same procedure as adopted for the normal constructional steels of similar tensile strength, and no special precautions are necessary.

Welding. The steels can be welded both by the electric-arc and oxy-acetylene processes, but on account of their air-hardening characteristics it

is necessary to preheat the material, preferably to a temperature of the order of 500° C, and to stress relieve after welding by cooling slowly from a temperature of approximately 650° C. Where it is impracticable to preheat and post-heat, cold welding may be employed, using high-alloy electrodes. The stabilized type of 18/8 Cr–Ni steel has been found satisfactory for this purpose. When using electrodes of this type it is generally advisable to use D.C. equipment with the electrode forming the positive pole. In the case of oxy-acetylene welding a borax-base flux is used. The various electrical-resistance methods of welding are also applicable to these steels, but it is desirable to normalize or reheat after welding, the heat treatment depending on the individual application. Forge or hammer welding is not applicable.

The steels are equally capable of being produced in the form of castings. Hot-rolled or cold-rolled tubes can also be produced, but owing to manufacturing difficulties associated with air-hardening steels, the non-air-hardening type is generally used for this purpose.

12 *to* 14 *per cent Chromium Steels.*

These are the well-known "stainless" or "rustless" iron and steel types, with carbon contents varying from 0·10 to 0·35 per cent. The general

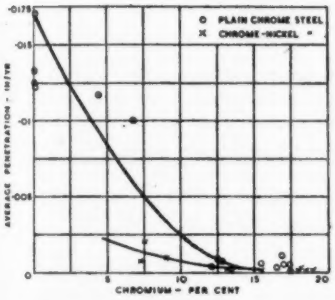

FIG. 31.

INFLUENCE OF CHROMIUM ON CORROSION IN CRACKING-COIL BUBBLE TOWER. (AFTER POLLOCK, CAMP, AND HICKS.)

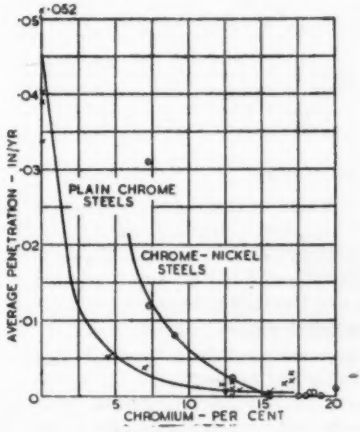

FIG. 32.

INFLUENCE OF CHROMIUM ON CORROSION BY CRUDE-OIL VAPOUR. (AFTER POLLOCK, CAMP, AND HICKS.)

trend of the curves already shown indicates the progressive improvement resulting from increasing additions of chromium, and Figs. 31 [14] and 32 [14] showing the effect of chromium content in increasing the resistance to corrosion in two types of petroleum-refinery conditions illustrate that under these conditions the optimum properties may be obtained with chromium in the range now being dealt with.

Whilst these steels have a good resistance to scaling up to temperatures

of approximately 750° C (Figs. 33 and 34,[21]), their hot strength is generally of the same order as that of a plain carbon steel.

The steels in this group, except for the "stainless" or "rustless" iron grades having a carbon content of less than 0·1 per cent, like those of the 4 to 6 per cent Cr group, are air hardening, and this tendency can be suppressed by additions of titanium or columbium. In order to develop their optimum properties they are oil or air hardened from 950° C, and tempered according to requirements.

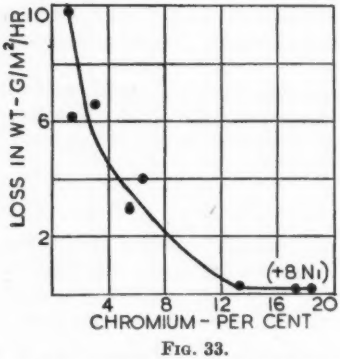

FIG. 33.

LOSS OF WEIGHT OF Cr-ALLOY STEELS IN A BROWN-COAL-TAR HYDROGENATION PLANT. (240 HR, 400–500° C, 300 ATM.) (AFTER NAUMANN.)

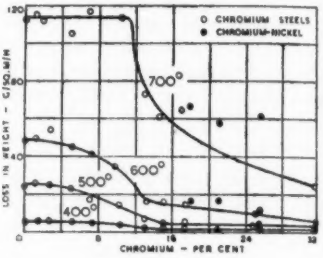

FIG. 34.

INFLUENCE OF CHROMIUM CONTENT ON THE SCALING OF STEEL ON HEATING IN H_2S (1 ATM PRESSURE). (AFTER NAUMANN.)

Fabrication.

Hot Working. On account of their lower thermal conductivity the "stainless" steels require considerably longer soaking than is usual for ordinary carbon steels. The forging temperatures employed vary between 1100° and 1200° C, and forging should not be continued after the temperature has fallen below approximately 900° C. Except in the case of the mildest grades (carbon 0·11 per cent) the tendency to air hardening may in some cases lead to cracking unless the material is slowly cooled after rolling or forging.

Cold Working. Between cold-working operations the steels should be softened by heating to 750° C and cooling in air. After cold working, this treatment, or quenching and tempering, is always desirable, as corrosion resistance is thereby improved.

Machining. Generally speaking these steels machine in very much the same way as tough alloy structural steels of the same order of tensile strength. As a class they have a tendency to drag, and it is advantageous slightly to increase the rake and cutting angles beyond those usually employed for ordinary steels. Free-machining grades can be produced by the introduction of a sulphur content in the range 0·25 to 0·40 per cent.[22] The disability of reduction in hot workability thereby introduced is stated by F. R. Palmer[23] to be overcome by the introduction of the sulphur as zirconium sulphide.

Welding. These steels can be welded by the usual fusion processes, but cannot be smith welded. No flux is necessary. The danger of cracks arising from welding can be greatly reduced by preheating to 200° or to 250° C, followed after welding by slowly heating to 650° or to 700° C, maintaining at this temperature until soaked, and then cooling in still air. The corrosion resistance of this type of steel is reduced by tempering at 475° to 595° C, and this range of temperature should therefore be avoided so far as possible.

30 per cent Chromium Steel.

The wide gap between the 30 and the 12 per cent chromium types discussed is taken up by the important group of austenitic corrosion- and heat-resisting steels containing 18 to 25 per cent chromium together with nickel and other added elements, which will be discussed later.

The 30 per cent chromium alloy is essentially a scale-resisting alloy, made in two grades, a soft grade containing up to 0·4 per cent carbon being used for forgings, and a hard grade containing 2 per cent carbon for castings. Both have a relatively low hot strength, the cast material being somewhat brittle when cold, *i.e.*, of the order of cast iron. The forged and rolled material is generally ductile, although it is notch brittle.

The alloy is highly resistant to oxidizing and sulphurous gases up to 1150° C. Temperatures of this order are rarely met with in the petroleum industry, and little comparative data is available to illustrate its superiority in this respect. One interesting experience may be referred to in connexion with its successful application in an experimental topping plant, in which the material ran continuously for three months at 1000° C without any signs of corrosion. Under the same conditions an 18/8 Cr–Ni type alloy had a life of only 1 month. Under less severe conditions of temperature, certain of the curves, B, C, and D already shown in Fig. 10 indicate its superior corrosion-resisting qualities, although in other cases (curve A) equal resistance is conferred by lower chromium additions.

From the results of the authors' scaling tests carried out under varying conditions at 950° and 1050° C and plotted in Figs. 15–19 the effect of chromium is apparent. Whilst there is still a definite trend indicating the over-riding influence of chromium, the wide scatter of results shown is due mainly to the effects of other added elements and methods of fabrication. In every case, however, the 30 per cent chromium-type steel will be found amongst the most highly resistant of the steels tested, and it is particularly interesting to note in Fig. 17 that with sulphur dioxide in the atmosphere the resistance is equally good whether the conditions are oxidizing or non-oxidizing. It will be seen from this chart that when non-oxidizing conditions are present together with SO_2, scaling is considerably increased in many alloys, particularly those containing nickel.

As already pointed out, a very prolonged exposure is necessary to obtain a true comparison of the scaling propensities of different steels. Nevertheless Fig. 35 constructed as a result of tests on chromium steels without the complication of added elements [24] is of interest as confirming the general effect of chromium noted in the authors' own charts in which are included chromium–nickel steels with their various modifications. In the tests referred to in this diagram, the specimens were exposed in dry commercial

oxygen under carefully controlled conditions at a temperature of 980° C for times up to 150 hours.

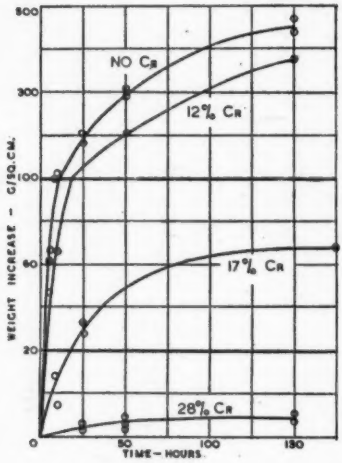

FIG. 35.

EFFECT OF CHROMIUM CONTENT IN PLAIN CHROMIUM STEELS ON SCALING IN DRY COMMERCIAL OXYGEN AT 980° C. (AFTER RICKETT AND WOOD.)

Fabrication.

Hot Working. Owing to its low strength at high temperatures the usual low-carbon forging grade is relatively easy to forge. It becomes stiffer, however, with increasing carbon. Owing to the tendency of the steel to grain growth and embrittlement the forging temperature is kept as low as possible, the initial temperature not exceeding 1150° C, and forging being continued down to approximately 800° C.

Cold Forming. The forging grade is reasonably ductile, and bars with smooth surfaces, for example, may with care be bent double, but owing to the notch brittleness referred to above, a nick or surface imperfection will cause it to break off short. For this reason it is safer to carry out any considerable deformation on the heated steel. The desirable range of temperature for this purpose is 750° to 900° C.

Machining. These alloys are much more difficult to machine than ordinary low-carbon steels, although in the annealed condition, even the hard grade used for castings is machinable. Low cutting speeds are necessary, however, for both grades.

Welding. Cast Material.—This is not normally weldable by the oxy-acetylene process, but can be welded by the electric arc process. Owing to the fragility of the high-carbon steel castings when cold, it is necessary to preheat before welding and to cool slowly after welding in order to prevent cracking. In the case of difficult shapes or dissimilar thicknesses the castings should be preheated to approximately 700° C, but when the welds are small in extent and not liable to set up cooling stresses of any great magnitude preheating to a temperature of 300° to 400° C will suffice.

D.C. equipment is preferred, using the electrode as the positive pole. The electrodes normally used are designed to give weld metal of a similar composition to the steel, but in certain applications it may be advantageous to use an austenitic electrode owing to its greater toughness.

The forged or rolled material can be welded by both processes. Whilst it has not the same fragility in the cold state as the cast material, it is advisable to preheat to 300° to 400° C and cool slowly after welding. Oxy-acetylene welding presents difficulties, but is possible with a suitable flux and a neutral or slightly reducing flame.

Although welds of this material are brittle at room temperatures it has been pointed out by Hodge [25] that they are quite ductile at 260° C or above, so that "welded structures may be employed at elevated temperatures without cracking in service."

18/8 *Chromium–Nickel Steels.*

As would be expected from the data already quoted, the corrosion resistance of this important group of alloys is greater than that found in the "stainless" group, as instanced by Figs. 5, 31, and 32, both because of the increase in chromium content and also by the addition of nickel. Table X, taken from Thum's book on stainless steels,[26] also shows the

TABLE X.

Corrosion Resistance of Steels in Petroleum Vapours at 175 lb Pressure and 340° C.[26]

Steel.	Loss by corrosion, mgm/sq. in/1000 hr.
18/8 Cr–Ni	2·1
12% Cr (0·12% C)	6·4
5% Cr (0·5% Mo) (cast)	47·0
5% Cr (1·0% W) (cast)	61·5
5% Cr (tube)	99·2
0·75% Cr (2% Ni) (cast)	153·0
Carbon steel (cast)	196·0

relative corrosion resistance to petroleum vapours at 175 lb pressure and 340° C of the steels so far discussed.

TABLE XI.

Composition of Steels referred to in Tables XII, XIII, XIV, and XV.

Steel.	C.	Si.	Mn.	Cr.	Ni.	W.	Cu.	Mo.	Al.	Ti.	V.
A	0·11	0·23	0·32	17·4	8·5	—	—	—	—	—	—
B	0·11	0·14	0·21	17·1	7·1	—	2·10	—	—	—	—
C	0·25	1·29	0·57	21·6	7·65	3·15	—	—	—	—	—
D [1]	0·17	0·45	0·33	17·7	8·1	3·50	1·98	—	—	—	—
D	0·20	1·50	0·89	19·8	7·0	3·76	1·90	—	—	—	—
E	0·09	1·06	0·56	18·9	9·4	—	—	2·35	—	—	—
F	0·15	0·28	0·24	18·3	8·4	—	2·23	3·48	—	—	—
G	0·19	1·25	0·80	21·4	7·1	—	—	—	—	—	—
H	0·15	0·68	0·62	19·5	8·4	—	—	—	—	0·80	—
I	0·15	0·39	0·30	17·4	9·55	0·69	—	—	—	—	—
J	0·19	0·44	0·61	19·0	8·1	—	—	—	—	—	1·04

TABLE XII.

Corrosion Test Results.

Sulphuric acid, cold—1 month.

Type of steel 18/8 +.	Steel.	Loss in grams per 100 sq. cm.				
		0·025% (0·044).	0·25% (0·44).	2·5% (4·40).	5·0% (8·80).	10·0% (17·60).
—	A	<0·01	<0·01	2·1	12·3	—
Cu	B	<0·01	<0·01	<0·01	< 0·01	1·90
Cr, W, Si	C	<0·01	<0·01	1·34	—	—
Cr, W, Cu, Si	D	<0·01	<0·01	<0·01	0·08	0·16
Ni, Mo, Si	E	—	<0·01	—	< 0·01	<0·01
Mo, Cu	F	nil	<0·01	<0·01	< 0·01	<0·01

TABLE XIII.

Corrosion Test Results.

Sulphuric acid, boiling 100 hours.

Type of steel 18/8 +.	Steel.	Loss in grams per 100 sq. cm.						
		0·025% (0·044).	0·25% (0·44).	0·5% (0·88).	1·0% (1·76).	2·5% (4·40).	5·0% (8·80).	10·0% (17·60).
—	A	0·17	1·24	3·23	9·90	24·7	30·0	—
Cu	B	0·09	1·27	3·65	7·05	15·4	Over 26·1	Over 30·4
Cr, W, Si	C	0·27	2·27	4·82	10·2	22·9	46·7	64·5
W, Cu	D [1]	0·08	0·50	0·60	1·45	2·8	3·3	31·3
Cr, W, Cu, Si	D	0·18	1·96	2·60	5·4	11·1	17·4	22·6
Ni, Mo, Si	E	0·13	0·91	1·12	1·5	2·7	9·3	23·7
Mo, Cu	F	0·09	0·40	0·74	1·2	2·1	7·0	14·6

TABLE XIV.

Corrosion Test Results.

Hydrochloric acid, cold and boiling.

Type of Steel 18/8 +.	Steel.	Loss in grams per 100 sq. cm.					
		Cold—1 month.			Boiling—100 hours.		
		1·0% (0·366).	5·0% (1·830).	1·0% (0·366).	5·0% (1·830).	10·0% (3·660).	1·1 sp. gr. 60%(22·0).
—	A	0·38	2·16	3·1	17·2	30·7	C.S.*
Cu	B	—	—	2·4	12·2	24·2	C.S.
Cr, W, Cu, Si	D	0·01	0·41	4·3	18·4	29·4	C.S.
Ni, Mo, Si	E	0·01	0·02	0·05	19·8	39·9	C.S.
Mo, Cu	F	0·01	0·02	0·01	1·1	7·1	C.S.

* C.S=Complete solution.

The addition of other elements such as silicon, tungsten, copper, and molybdenum have been discussed by one of the authors (R.J.S.) in a previous paper,[27] and they have a marked effect on the resistance to specific corroding agents, as can be seen from Tables XI, XII, XIII, and XIV.

The ordinary 18/8 type is only usefully resistant to sulphuric acid, for example, in cold and very dilute solutions. The addition of molybdenum and copper in particular, however, appears to be of advantage in this respect. The same elements, together with tungsten (steel D[1]), have a markedly beneficial effect in promoting resistance to boiling sulphuric acid. Molybdenum also appears to improve the resistance to hydrochloric acid, as shown by Table XIV, steel F in particular, containing both molybdenum and copper, showing considerable improvement over the plain 18/8 material.

Although primarily resistant to corrosion, the alloys in the 18/8 class are highly resistant to scaling and creep up to temperatures of 800° C. An interesting series of curves showing the value of the higher chromium in this connexion is shown in Fig. 34 already referred to in the section on 12 per cent Cr steels.

A well-known disability of the plain 18/8 Cr–Ni steels is the susceptibility to corrosion brittleness and weld decay, both of which arise from heating in the range 450° to 900° C. A brief indication of the nature of these defects may be of interest here, although they have been discussed in more detail elsewhere, including an earlier paper with which one of the authors was associated.[27]

Corrosion Brittleness.

On heating 18/8 Cr–Ni type steels in the temperature range mentioned, carbides are precipitated at the grain boundaries, and if a specimen containing these carbides is subjected to the action of a corroding agent of an oxidizing nature, it becomes quite brittle as shown by steel A in Table XV. With material which has been cold worked and afterwards exposed to the harmful temperature range, the precipitation occurs not only at the grain boundaries, but also within the grains, in the slip planes resulting from the cold working. Material which has been rendered potentially corrosion brittle by heating, but has not been exposed to the action of the corroding agent, can be completely restored to its original condition by reheating to a temperature of say 1150° C, thus redissolving the precipitated carbides.

Weld Decay.

Deterioration of the steel also arises as a result of welding, when a narrow zone of material, commencing about $\frac{1}{2}$ in from the edge of the weld on either side, is found to be much more susceptible to corrosion than the remainder.

Causes and Prevention of Intergranular Corrosion.

The exact relationship between weld decay and corrosion brittleness is still somewhat obscure. Both are conditions of potential liability to intergranular corrosion resulting from heating at some temperature between 450° and 900° C. Weld decay is induced in a few minutes, however, since the time of exposure to the high temperature in the course of operation is very short. On the other hand, heating for many hours may be necessary to develop corrosion brittleness. The following theory, held by the authors, would account for corrosion brittleness, and at the same time provide the link with weld decay. The normalized material has an austenitic structure free from carbide, the austenite being supersaturated with respect to

TABLE XV.

Corrosion Brittleness Tests.

Effect of modifications of the composition of the 18/8 type steel.

Bend test results after 17 hours' immersion in the test solution on specimens quenched in water from 1150° C, and reheated at various temperatures.

Material used: Forged bar $\frac{3}{8}$-in by $\frac{1}{16}$-in section.

Type of steel 18/8 +.	Steel.	As quenched from 1150° C in water.	Reheating temperature and time held at temperature.															
			500° C.			570° C 100 hr.	600° C.			700° C.		800° C.				900° C.			
			10 min.	50 hr.	100 hr.		10 min.	50 hr.	100 hr.	10 min.	50 hr.	10 min.	50 hr.	5 min.*	1 hr.*	10 min.	50 hr.	5 min.*	1 hr.*
—	A	U	U	D	B	E	C	E	E	D	U	U	U	U	U	U	U	U	U
Si	G	U	U	C	—	—	B	C	—	B	U	U	U	—	—	U	U	—	—
Ti	H	U	U	U	U	U	U	U	U	U	U	U	I	—	—	U	U	—	—
W	I	U	U	E	—	—	C	D	—	E	A	U	U	—	—	U	U	—	—
V	J	U	U	U	U	A	U	A	B	U	U	U	U	—	—	U	U	—	—

U—Uncracked.
A—Very slightly cracked.
B—Slightly cracked.
C—Badly cracked.
D—Very badly cracked.
E—Broken.

* Additional tests on steel A.

carbon. Reheating at temperatures lower than 800° C results in precipitation of carbide at the grain boundaries. This carbide is rich in chromium, and for its formation denudes the immediately adjacent matrix of some chromium. As diffusion is very slow, this denuded area remains lower in chromium. The denuded zone can, and does in many instances, become so low in chromium that it cannot remain austenitic in the cold, and therefore it reverts to the α condition (usually martensite) with change of volume. Hence the grain boundaries are in a state of strain, and it is this fact, in the authors' opinion, that creates the condition whereby very rapid disintegration occurs when subjected to corrosive attack. Without the strain, the reduced resistance to corrosion resulting from the lowered chromium content would only lead to a low rate of attack, and not to the rapid boundary disintegration which is so characteristic of corrosion brittleness.

It is of interest that 18/8 Cr–Ni steel becomes subject to corrosion brittleness on heating for a short time at 700° C, but by a long soaking (50 hours or more) at this temperature it again becomes immune, as shown in Table XV. The explanation of this is attributed to rediffusion of chromium from the matrix into the denuded areas, the temperature of 700° C being high enough and the chromium content sufficient to reconvert these areas into austenite, which is stable at room temperatures. The carbide originally precipitated remains still out of solution, usually as coarser globules than when heated for only a short time. Hence it is not carbide alone which renders material corrosion brittle. This theory, postulating a condition of stress as an essential factor, would also explain the occurrence of weld decay, since in this case the stresses would arise immediately as a result of the welding operation.

The effect of the addition of various elements on the liability of these steels to corrosion brittleness was investigated and Table XV shows that the addition of 0·80 per cent Ti entirely inhibits corrosion brittleness, and 1 per cent V appreciably limits the range of temperature within which the trouble is caused.

Fabrication.

Hot Working. This material can be produced both as castings and forgings. In spite of its much greater stiffness and rigidity than ordinary steels at high temperatures, it can be forged or rolled into the usual sections, bars, rods, plates, sheets, tubes, etc. Forging is carried out at temperatures between 1180° and 900° C, keeping as near to the upper limit as possible. Owing to the low thermal conductivity of the material it is necessary for the billets to be soaked for at least twice as long as ordinary steels. The soaking is applied preferably at a temperature of approximately 950° C, after which it is quickly raised to the forging temperature and soaked for a short time before commencing forging. A further point of significance in the hot working of these high-alloy steels is that their thermal expansion is approximately 50 per cent greater than that of mild steel.

After forging it is usual to reheat to 1150° C and cool quickly, in order to put it into its best condition for resisting corrosion.

Cold Working. In the softest condition, which is obtained by rapid cooling from 1150° to 1200° C, the material can readily be cold drawn or

TABLE XVI.

Results of Scaling Tests at 950° C. Arranged in Order of Resistance to Sulphur-Containing Oxidizing Atmosphere.

No.	Type.			Analysis.							Loss in weight due to scaling, gm/100 sq. cm.			
	Cr.	Ni.	Other elements.	C.	Si.	Mn.	Cr.	Ni.	W.	Al.	3000 hr electric in air.	3000 hr gas furnace.	3000 hr sulphur-containing atmosphere.	880 hr at 950° C in a non-oxidising atmosphere + SO_2.
1	20–	7	W, Al	0·37	1·42	0·56	20·7	7·0	3·93	5·7	0·60	0·45	0·26	0·5
2	,,	,,	Si, W	0·35	3·40	0·52	20·0	7·0	4·03	—	2·98	3·06	0·81	3·4
3	25–	18	Si	0·21	2·99	0·68	25·8	18·2	—	—	—	1·12	0·88	22·2
4	20–	7	Si	0·30	3·55	0·78	20·3	7·2	—	—	6·5	4·5	0·99	18·1
5	30–	0		0·35	0·75	0·30	29·0	—	—	—	3·6	2·55	1·07	3·6
6	20–	60	Si	0·38	2·15	1·30	19·4	58·7	—	—	1·56	1·52	1·13	54·7
7	25–	12	Si	0·24	3·4	0·94	24·5	12·2	—	—	—	1·06	1·14	2·5
8	,,	,,	Si, W	0·33	1·54	0·53	24·8	12·2	3·97	—	3·60	3·55	1·50	28·1
9	25–	20	Si	0·12	1·42	0·65	24·5	20·4	—	—	—	—	1·59	57·7
10	16–	35	Si, W	0·49	1·88	0·82	16·4	35·0	1·45	—	5·2	2·43	1·72	68·0
11	25–	12	Si	0·22	1·84	0·98	25·7	12·2	—	—	7·7	4·35	1·90	43·1
12	25–	18	Si	0·13	1·92	0·57	25·8	17·6	—	—	4·05	2·55	1·92	42·9
13	14–	28	Si, W	0·30	1·25	1·25	14·0	28·0	4·0	—	25·5	10·7	3·15	54·8
14	25–	12	Si	0·24	0·98	0·86	24·5	12·1	—	—	—	6·05	3·33	35·5
15	20–	7	Si, W	0·35	1·25	0·50	20·7	7·0	4·0	—	19·3	18·0	6·27	49·2
16	,,	,,	Si	0·18	1·52	0·51	20·4	7·2	—	—	13·6	20·1	6·95	37·7
17	12–	60	Si	0·34	1·30	1·94	11·5	59·2	—	—	3·14	2·78	13·2	132·0
18	18–	8		0·07	0·12	0·48	17·5	8·8	—	—	121·0	121·0 (after 325 hrs)	121·0 (after 1368 hrs)	63·7
				No. of Temperature Cycles							59	17	17	6
				Analysis of Atmosphere:										
				CO_2							—	4·0	4·7	7·0
				O_2							—	12·4	11·0	Trace
				CO							—	Nil	Nil	5·0
				SO_2							—	0·003	0·043 (≡1·5% S coal)	0·043
				Unsaturated hydrocarbons							—	—	—	Trace

cold pressed. This operation naturally work hardens the material, and it may be found necessary to anneal between successive stages of the operation. Heating to 950° C followed by air cooling will generally suffice for this purpose. The final treatment should be to heat to 1150° to 1200° C and air cool, in order to develop the optimum corrosion-resisting properties.

Machining. Both castings and forgings are readily machinable, but as the material is tougher than ordinary steels slower cutting speeds should be used.

Welding. The material can be welded readily by the usual fusion-welding processes, and it is usually unnecessary to preheat. In the case of castings of complicated shapes or dissimilar thicknesses it may be advisable to preheat to a temperature of 200° to 300° C, and slowly cool after welding. In addition, owing to the susceptibility to weld decay already mentioned, the non-stabilized type of material should be reheated after welding to a temperature of at least 1050° C and cooled quickly. This treatment is usually unnecessary in the case of the stabilized types of material, although it may be advisable in the case of complicated structures in order to relieve the stresses set up in welding. Air cooling is satisfactory for the lighter sections, but water quenching is advisable for heavier sections, say $\frac{3}{16}$ in and over. D.C. equipment is preferred, the electrode forming the positive pole. When using the oxy-acetylene process an uncoated wire rod of the same composition as the material to be welded is suitable, and it is not normally necessary to use a flux, provided a neutral or slightly reducing flame is used.

Highly Alloyed Austenitic Steels.

Intermediate in chromium content between the 18/8 Cr–Ni alloys used primarily for corrosion resistance and the 30 per cent chromium scale-resisting material lies the wide range of heat-resisting alloys possessing such excellent qualities as regards scale resistance, strength at high temperatures, and toughness and ductility at atmospheric temperatures. A representative selection has been included in the curves already shown illustrating the effect of chromium on scaling. The main types are the 21/7, 25/12, 25/18, 12–20/60 Cr–Ni alloys, all of which may be modified by additions of other elements such as silicon, tungsten, aluminium, etc.

In Table XVI is shown the loss in weight resulting from scaling at 950° C in various atmospheres for a number of these steels, together with an 18/8 and 30 per cent chromium steel for comparison. The steels are arranged in order of merit as regards resistance to scaling in an atmosphere of town's gas containing SO_2. In the tests referred to the specimens were withdrawn, air cooled, wiped to remove loose scale, and weighed, at regular intervals until the total period of 3000 hours had elapsed. Typical curves illustrating the progress of scaling in one such series of tests are shown in Fig. 36 from which certain general features are obvious.

The scaling losses found in the series heated in air are generally higher than those resulting from heating in burnt town's gas. This is ascribed to the higher partial pressure of oxygen together with the larger number of temperature cycles employed, namely fifty-nine for the former compared with seventeen for the latter series. The addition of sulphur dioxide to the burnt town's gas, which was of an oxidizing nature, increased the scaling

of the high-nickel steel 17, but in general reduced the scaling of the others. This observation is in line with work reported by Camp, Phillips, and Gross[28] who added sulphur to the corrosive medium in order to reduce scaling of 18/8 furnace tubes in high-temperature vapour-phase cracking service. The greatly increased amount of scaling resulting from the use of a reducing atmosphere in the presence of sulphur dioxide is apparent.

Steels containing nickel of the order of 60 per cent are amongst the most resistant of the series heated in air or burnt town's gas, but their resistance is considerably reduced when sulphur dioxide is added to the atmosphere, particularly under reducing conditions. On the other hand, the 30 per cent chromium steel and the steel containing aluminium is hardly affected. The effect of the condition of the atmosphere when SO_2 is present tends to

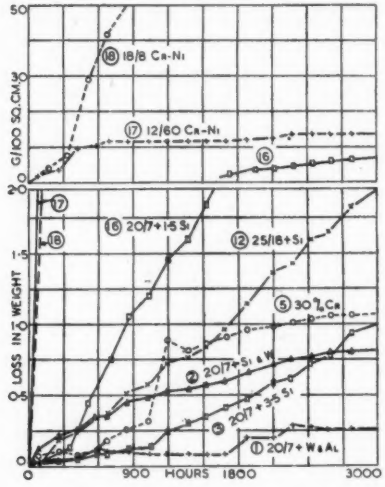

FIG. 36.

TYPICAL CHART SHOWING PROGRESS OF SCALING OF DIFFERENT STEELS AT 950° C. (3000 HR IN SULPHUR-CONTAINING ATMOSPHERE.) THE RINGED NUMBERS REFER TO TABLE XVI.

become more marked as the nickel content increases, as shown in the earlier Fig. 18.

The effect of the various elements added in addition to the chromium and nickel is illustrated in Table XVII, which applies to a temperature of 950° C and the various atmospheres shown.

Under the conditions applying, the addition of aluminium considerably reduces the rate of scaling; the addition of silicon in the presence of nickel is beneficial, but has little effect when nickel is absent, and additions of tungsten are in general accompanied by a slight increase in resistance to scaling. It should be emphasized again, however, that these results apply only to the conditions obtaining in the tests.

The same general picture is obtained in Fig. 19 in regard to the tests carried out in burnt town's gas at 1050° C, the 18/8 type being the least

TABLE XVII.

Effect of Added Elements on the Scaling of Austenitic Chromium–Nickel Steels.

Special element.	Analysis.							Loss in weight (g/100 sq. cm at 950° C.)			
								After 3000 hours.			After 800 hours.
	C.	Si.	Mn.	Cr.	Ni.	W.	Al.	Electric furnace, air.	Burnt town's gas.	Burnt town's gas + SO_2 oxidising.	Burnt town's gas + SO_2 non-oxidising.
Silicon	0·21	2·99	0·68	25·8	18·2	—	—	—	1·12	0·88	22·2
	0·13	1·92	0·57	25·8	17·6	—	—	4·05	2·55	1·92	42·9
	0·24	3·4	0·94	24·5	12·2	—	—	—	1·06	1·14	2·5
	0·22	1·84	0·98	25·7	12·2	—	—	7·7	4·35	1·90	43·1
	0·24	0·98	0·86	24·5	12·1	—	—	—	6·05	3·33	—
	0·35	3·40	0·52	20·0	7·0	4·03	—	2·98	3·06	0·81	3·4
	0·35	1·25	0·50	20·7	7·0	4·0	—	19·3	18·0	6·27	49·2
	0·30	3·55	0·78	20·3	7·2	—	—	6·5	4·5	0·99	18·1
	0·18	1·52	0·51	20·4	7·2	—	—	13·6	20·1	6·95	37·7
	0·17	2·1	0·62	28·5	—	—	—	—	3·02	1·80	3·9
	0·35	0·75	0·30	29·0	—	—	—	3·6	2·55	1·07	3·6
Aluminium	0·37	1·42	0·56	20·7	7·0	3·93	5·7	0·60	0·45	0·26	0·5
	0·35	1·25	0·50	20·7	7·0	4·0	—	19·3	18·0	6·27	49·2
Tungsten	0·35	3·40	0·52	20·0	7·0	4·03	—	2·98	3·06	0·81	3·4
	0·30	3·55	0·78	20·3	7·2	—	—	6·5	4·5	0·99	18·1
	0·35	1·25	0·50	20·7	7·0	4·0	—	19·3	18·0	6·27	49·2
	0·18	1·52	0·51	20·4	7·2	—	—	13·6	20·1	6·95	37·7
	0·33	1·54	0·53	24·8	12·2	3·97	—	3·60	3·55	1·50	28·1
	0·22	1·84	0·98	25·7	12·2	—	—	7·7	4·35	1·90	43·1

resistant, and the 30 per cent chromium and 60 per cent nickel alloys amongst the most highly resistant. Again aluminium and silicon are beneficial. Tungsten appears to have little influence on the resistance to scaling under these conditions.

It should be mentioned here that special elements are added not only with the object of conferring increased resistance to scaling, but also with the intention of improving such properties as hot strength, castability, etc., and resistance to specific corroding media.

Fabrication.

Hot and Cold Working. In general what has been said with regard to the 18/8 chrome–nickel and 30 per cent chromium steels applies equally well to this group of alloys. As regards forging, they are probably somewhat stiffer than the 18/8 type and the temperatures used are kept within the rather narrower range of 1150° to 950° C. Being ductile, they can be cold worked, but harden up during the operations.

Machining. In machining the heat-resisting steels a slightly heavier cut is advisable than is employed for the 18/8 alloys, other conditions remaining the same.

Welding. No preheat is necessary in welding except for the 60 per cent nickel alloys, which in the case of rigid joints are preheated to 300° to 400° C and slowly cooled after welding.

Conclusions.

1. The paper reviews the effect of composition and methods of fabrication on the behaviour of steels as used in the petroleum industry. The causes of corrosion therein encountered and methods of overcoming its effects are discussed in special reference to the composition of the steel.

2. The economic limit of chromium content permissible in plain chromium steels depends upon service conditions. In respect of corrosion in industrial atmospheres, a wide range of tests has been correlated to show the quantitative influence of chromium in low-carbon compositions. Corrosion due to salt water in condenser boxes shows the normal optimum of 13 per cent chromium in plain chromium steels, and a recognized specific optimum in the case of the 18/8 type chromium–nickel alloys. Behaviour in service in refineries varies widely with refinery conditions.

3. In medium-pressure-steam corrosion in the presence of hydrogen sulphide (4 per cent) a hyperbolic relation between corrosion and chromium content is shown to exist, the presence of the liquid phase markedly increasing the corrosion.

4. The influence of sulphur dioxide under oxidising and reducing conditions has been investigated in town's gas atmospheres in the range of temperature 450 to 1050° C for both plain chromium steels containing up to 6 per cent chromium, and for alloyed steels containing up to 30 per cent chromium. In the presence of appreciable quantities of sulphur dioxide there appears to be a temperature of the order of 750° C at which a transition occurs in the relative influence of sulphur dioxide on scaling; below 750° C the sulphur dioxide is more active than the oxygen; above 750° C the reverse is the case. At 950° C, with alloyed steels containing 10 to 30 per cent chromium and varying contents of nickel, the rate of scaling for normal industrial contents of sulphur dioxide occurring in burnt fuel gases is increased some ten times by a change from oxidizing to reducing conditions, the exact ratio of this change depending upon the content of nickel in the alloy. At temperatures above 750° C the specific influence of additional special elements may become predominant in determining the rate of scaling under both oxidizing and reducing conditions. At temperatures of 1050° C the general statements above are still valid; the addition of other elements such as aluminium becomes desirable for scale-resisting reasons, but causes difficulties in fabrication.

5. At high temperatures, the effect of creep also becomes of importance, and examples are given of the effect of additions of elements such as molybdenum and vanadium to increase the creep strength.

6. In the fabrication of steels the additions of alloying elements may cause trouble or increased difficulties in manufacture, so that certain methods of production, such as forging, may be difficult or impossible. The manufacture of castings has, however, progressed enormously since the beginning of the war, and with proper care, such as the use of radiographic examination, they may replace other methods of production especially for intricate designs. Examples are given of the standards already attained by special highly stressed castings, and consideration is given to the role which they could play in the petroleum industry in the future.

7. The susceptibility to corrosion brittleness and weld decay of the 18/8

type of steel is known to be overcome by the addition of titanium or vanadium. The usual theory of the causes of weld decay and corrosion brittleness is shown to be inadequate, and modifications involving considerations of stress conditions arising from carbon precipitation are suggested, which make the explanation more reasonable.

The detailed examination of the effect of numerous additions of alloying elements is the specialized province of the steel manufacturer. There is scope for the users of steel in the petroleum industry to define more precisely the conditions of service. This involves the application of extensive field trials made in collaboration with the steel manufacturer. The use of statistical methods of analysis are recommended in this context.

Acknowledgments.

The authors wish to express their thanks to the directors of Messrs. Hadfields, Ltd, for permission to publish this paper. To the other members of the Research Department, particularly T. H. Middleham, J. Arnold, G. Wood, and H. Newman, who have assisted in the preparation of the data and other details of the paper, the authors express their grateful appreciation.

References.

[1] Thum. "The Book of Stainless Steels." A.S.M., Cleveland, 1935, p. 20.
[2] Thum. *loc. cit.*, p. 24.
[3] Marsh. "Alloys of Iron and Nickel," Vol. 1. McGraw-Hill Book Co., p. 53.
[4] Thum. *loc. cit.*, p. 47.
[5] Jeavons and Pinnock. *Gas J.*, 1930, **191**, 203, 255.
[6] Mudd. *Corrosion*, Dec. 1945, pp. 192–218, March 1946, p. 25.
[7] Vernon. *J. Sci. Inst.*, 1945, **22** (12), 225.
[8] Pfeil. *J. Iron Steel Inst.*, CXXIII, 1931, **123**, 237.
[9] Uhlig. *Chem. Engng News*, 1946, **24**, 3154.
[10] Jackson and Quarrell. *Iron Steel Inst. Special Report* No. 24 (1939), 65.
[11] Hickman and Gulbransen. *A.I.M.E. Metals Tech., Tech. Publ.* 2069, Oct. 1946.
[12] Preece, Richardson and Cobb. *Iron Steel Inst. Special Report* No. 24 (1939), p. 9.
[13] Marsh. *loc. cit.*, pp. 495–497.
[14] Pollock, Camp and Hicks. *A.I.M.E. Tech. Publ.* 639, Feb. 1935.
[15] Wright. *World Petrol*, Oct. 1937, 158.
[16] Jackson. *J. Iron Steel Inst.*, 1945, 225 p.
[17] Keating. *Iron Steel Inst. preprint*, Aug. 1946.
[18] Thum. *loc. cit.*, p. 236.
[19] Habart. *Metal Progress*, April 1940, p. 401.
[20] Wilson. *Metal Progress*, Sept. 1935, p. 29.
[21] Naumann. *Tech. Mitt. Krupp*, 1938, **4**, 77.
[22] Thum. *loc. cit.*, pp. 277 and 261.
[23] Palmer. *Trans. A.S.S.T.*, 1928, **14**, 877–892, 950.
[24] Rickett and Wood. *Trans. A.S.M.*, 1934, **22**, 347–384.
[25] Thum. *loc. cit.*, pp. 194–197.
[26] Thum. *loc. cit.*, p. 248.
[27] Elliot, Sarjant, and Cullen. *J. Soc. chem. Ind.*, 1932, **51**, 502–514, 527–531.
[28] Camp, Phillips, and Gross. *Corrosion*, Sept. 1945, p. 149.

SOME MODIFICATIONS OF THE LAMP METHOD FOR THE DETERMINATION OF SULPHUR IN PETROLEUM PRODUCTS.

By George E. Mapstone * (Member).

Summary.

Burning rates of up to 19 g of gasoline per hour have been achieved by modifying the chimney of the lamp sulphur apparatus, the standard absorber being quite efficient at the higher rates. A simple modification of the lamp is also described which enables greater burning rates to be obtained with kerosine samples.

With the standard lamp method for the determination of the sulphur content of gasoline (I.P. Method 62/42) the sample is burned for 1 to 1½ hours at the rate of 2 to 2½ g per hour. A faster method using an elaborate lamp and absorption train has been developed (I.P. Method 107/45T), which is capable of burning 20 g of sample per hour. In order to speed up the determination and still retain the simplicity of the former method for routine testing, some of the factors affecting the rate of combustion of the sample were examined, and the test modified to take advantage of any improvements while retaining its essential simplicity.

The Chimney.

Increasing the suction applied to the absorber drew the flame farther up the chimney with subsequent increase in the burning rate; but the position of the wick in the centre of the chimney was increasingly critical under these conditions. Lowering the lamp so that the wick was about 1 cm below the chimney assisted control, but the flame still showed a great tendency to give a fine feather of smoke, and thus invalidate the analysis. With this technique the burning rate could be increased to about 10 g per hour but, at this rate, approximately three-quarters of the lamps smoked during the test, and about half smoked when burning rates were increased to only 5 or 6 g per hour.

In order to increase the turbulence in the gases in the combustion zone a minor but effective alteration was made to the chimneys by constricting the basal opening to create a venturi effect. With this modification it was immediately possible to burn over 10 g of gasoline per hour without smoking. At the same time the position of the lamp was not as critical as with even the standard method, and the tendency to smoke was very greatly reduced. With the final chimney (Fig. 1) the lamp was placed so that the top of the wick was 8 to 10 mm below the chimney, and could be placed as much as 1 cm off centre without seriously affecting the flame. The flame was very thin as it entered the chimney, but flared to a brush at the top in contrast with the thin flame obtained with the plain chimney.

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Various chimney sizes were examined and smoothest operation was obtained with a 5 to 7 mm diameter orifice in the base. Increasing the internal diameter of the chimney did not affect the efficiency, but the increased weight was a disadvantage. Also the heat of the flame occasionally cracked chimneys of heat-resistant glass of less than 20 mm internal diameter, so 22 to 25 mm was adopted as standard. Making the modified chimney calls for but little more glass-working skill than does the standard chimney.

With the higher burning rates obtainable with this venturi chimney, the greater quantity of hot gases entering the absorber frequently completely

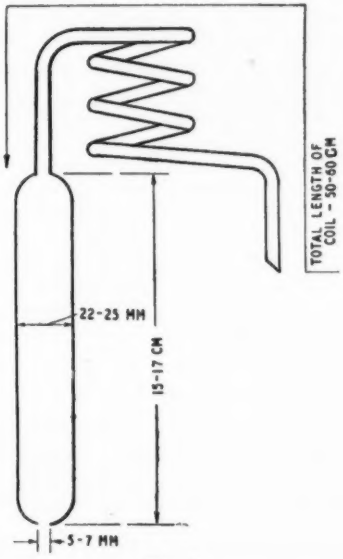

FIG. 1.

VENTURI CHIMNEY FOR SULPHUR DETERMINATION LAMP.

evaporated the absorbent solution in 10 to 15 minutes. A convenient air cooler was incorporated with the chimney by increasing the length of glass tube between the barrel and the absorber. 20 to 24 in was a suitable length, and it was most conveniently arranged in three horizontal coils before entering the adsorber (Fig. 1). With this air cooler less evaporation of the absorbent solution was experienced than with the standard test, even when the burning rate was as high as 15 g per hour.

Control of the flame with the necessary increased air-flow rate was best maintained by the screw clip between the splash trap and the suction manifold. Control was more readily maintained when the manifold suction was at least 12 in water gauge.

When using the venturi chimney, burning rates of less than approximately 5 g of gasoline per hour were difficult to maintain, as the flame was readily

drawn off the wick by the suction effect. Steady control was obtainable with burning rates of 6 g of gasoline or more per hour.

With samples which could be burned at rates of over 2 g per hour use of the venturi chimney gave easier control, but below that rate the normal chimney was the better.

In order to check the effect of the greater flow rate through the absorber on the adsorption efficiency, a sample of gasoline was analysed using the standard method and then the venturi chimney at various burning rates. The results, which are given in Table I, indicate that the standard absorber was quite efficient with the higher flow rates, and that the use of the venturi chimney caused no observable change in the accuracy of the analysis.

TABLE I.

Comparison of Normal and Modified Methods.

(a) Standard method. Mean of three analyses, 0·199 per cent S.
(b) Venturi chimney:

Burning rate, g/hr.	Sulphur, per cent.
5·7	0·194
5·7	0·193
7·8	0·201
9·8	0·199
11·7	0·194
11·8	0·196
15·2	0·198
18·9	0·196
Mean	0·196

Use of the venturi chimney reduced, but did not completely eliminate, the tendency to smoke of highly aromatic samples. With benzole, for example, the flame flared as usual with this type of chimney but, even with the most careful control, the chimney started to soot up after about 5 minutes' burning.

For a period of over twelve months in a refinery laboratory the standard and the venturi chimneys have been used interchangeably for the routine determination of the sulphur content of gasoline samples without any significant variation between the two methods being observed. Ten different operators with experience with both methods unanimously report a strong preference for the venturi chimney because of the greater ease of control as well as the increased burning rate obtainable.

THE LAMP.

(a) *Wick.*

When oxidized gasoline samples are burned in the normal lamp a deposit of gum and carbon on the wick can seriously affect the test. It was found that a wick of long fibre glass wool (an occasionally enforced wartime substitute for the standard cotton wicking) gave excellent burning characteristics and less gum and carbon trouble with high gum-content gasolines. The only characteristic trouble experienced with these glass-wool wicks

was the tendency of the tips of the fibres to fuse if the wicks were raised too high into the flame. This fault was not very great, and was readily minimized by careful trimming of the fibres before use.

Heavy oil samples which badly charred the cotton wicks could frequently be burned in a lamp with a glass-wool wick, though the operation was not necessarily trouble free, other factors being significant with some samples.

(b) *Heavy Samples.*

The application of the lamp method for the determination of the sulphur content of petroleum products is limited by the viscosity and volatility of the sample. Increasing the temperature of some heavy samples could render them capable of being analysed by this method.

Surrounding the glass tube holding the wick with a short length of copper tubing extending from just below the flame to above the oil level in the lamp increased the rate of burning appreciably. This effect appeared to be due almost entirely to the reduction of the viscosity of the oil ascending the wick.

Heavy gasoline fractions and kerosine samples could be burned faster if a " copper " lamp were used, but it was unsuitable for normal gasoline samples as the flame was far too large and difficult to control.

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THE TWO-STAGE IGNITION OF HIGHER HYDROCARBONS AT ATMOSPHERIC PRESSURE.

By G. FRIEDLANDER and L. GRUNBERG (Fellow).

SUMMARY.

Ignition experiments were carried out with a Moore type apparatus in the "low-temperature region." With *n*-heptane, ignition was found to be preceded by a "pre-ignition pulse," which persisted even at temperatures at which ignition did not yet occur. With *n*-heptane–benzene mixtures three distinct regions were observed. Between a high-temperature region characterized by ignition and a low-temperature region in which only the pre-ignition pulse occurs, there exists a region in which only slow oxidation takes place.

Gas samples were collected at different stages of the reaction and were analysed for CO, CO_2, O_2, C_nH_{2n}, alkyl–hydrogen peroxides, and aldehydes. The decline of an alkyl–hydrogen-peroxide maximum was found to be responsible for the "pre-ignition pulse."

A theoretical explanation of a chain reaction in accordance with the experimental results is presented. The products of decomposition of the pre-ignition pulse may either follow a branching reaction or degradation reactions. Benzene acts mainly by withdrawing the OH-chain carriers from the heptane reactions.

INTRODUCTION.

THE "low-temperature" region of ignition of the higher paraffin hydrocarbons is of importance since it comprises the temperature range within which knocking occurs in internal-combustion engines. In this region slow oxidation, "cool flames," and two-stage ignition are evident. The relations of these phenomena to temperature and pressure follow a complicated mechanism which has not yet been completely elucidated, and the present paper deals with research work on this subject. For details of the state of present-day knowledge, reference should be made to standard works or symposia.[1, 2, 3, 4]

The methods of investigating the ignition properties of liquid motor fuels are limited. Gaseous fuels such as methane, ethane, and propane can be investigated by flow or static methods, using a mixture of gas with air or oxygen, but such methods are not readily applicable to liquid fuels. In order to obtain gas mixtures which contain a sufficient amount of vaporized fuel, the mixture must be kept at elevated temperatures which, although well below the temperature at which noticeable reactions proceed, may still be high enough to create a number of active centres with a considerable influence on the course of the reaction. It was, therefore, decided to use a method by which liquid fuel is introduced into a crucible kept at a definite temperature. The error caused by a portion of the crucible being cooled by the sudden vaporization of the fuel can be minimized by using so little fuel that its heat of vaporization is small in proportion to the total heat capacity of the system. The principle is used in the so-called "oil-drop" method first used by H. Holm.[5] Based on it H. Moore [6] developed an ignition apparatus, which was subsequently modified by other workers. According to this method a drop of fuel is introduced into a crucible kept at a definite

temperature and a stream of air or oxygen of the same temperature is passed into the crucible at a definite rate. The time lag between the entry of the drop into the crucible and ignition is measured for every temperature. The " spontaneous-ignition temperature " of the fuel is defined as the lowest temperature at which ignition can still be observed. Various types of apparatus and experimental procedures are employed by different workers leading to a certain amount of disagreement in results. C. W. Sortman, H. A. Beatty, and S. D. Heron,[7] who also found that " zones of non-ignition " exist with *n*-heptane and cetane, observed that the rate of flow of air and the drop size influenced the results obtained with a Moore type apparatus. This is readily understood by the fact that the experiments were carried out in the " low-temperature " region of ignition, in which small variations in mixture strength and pressure affect the relation between ignition delay and temperature and decide whether ignition is possible. The " zones of non-ignition " correspond to the non-ignition peninsula on the temperature–pressure diagram, as observed by D. T. A. Townend.[8]

In spite of these disadvantages and difficulties, the Moore apparatus offers the advantage that a great number of readily repeatable results may be obtained. It is, however, essential to standardize all conditions under which the experiments are carried out. By doing so it becomes possible to relate the physical phenomena to the chemical changes occurring in the gas mixture, and the experimental procedure adopted in the present work is an attempt to achieve this correlation. In the opinion of the authors, it is important to keep the mixture strength constant during the course of every experiment, and for this purpose only the volume of air contained in the crucible without any flow was used. In addition, a standard procedure for the slow formation of the drop from the feed-burette was adopted, so that at any one temperature a constant mixture strength was obtained.

In preliminary experiments in which the most suitable design of apparatus and experimental procedure was established, another phenomenon besides ignition was observed. Under certain conditions a sudden expulsion of vapour from the crucible occurred. Immediately prior to ignition and also at temperatures at which no ignition took place this *pre-ignition pulse* was recognized as the first stage in the now well-established process of two-stage ignition.[9] It is interesting to note that Prettre [10] reported the presence of " fogs " (dense vapours) of reactive substances in oxidation experiments. Accumulation of these vapours was followed by explosion, whilst dispersion led only to the formation of " cool flames." Prettre suggested that the reactivity of the vapours was due to the presence of peroxides and, as will be shown in the course of this paper, the vapours expelled during the pre-ignition pulse were found to contain a relatively high proportion of alkyl–hydrogen peroxides and are probably identical with the dense vapours observed by Prettre. The appearance of " cool flames " immediately after the pre-ignition pulse was also observed in the crucible.

Description of Apparatus.

The apparatus used (Fig. 1) consists of a silica crucible (1) (60 cc capacity) which is partially immersed in a lead bath (2) contained in an electric furnace (3). The silica crucible is covered and held firmly in position

by a screw lid (4) with four apertures. The crucible can be scavenged of the products of combustion with hot air passing through the pipeline (5). The gas mixture is sampled through the capillary tube (6). The pre-ignition pulse is observed by means of an inclined glass tube manometer (7) which is filled with a drop of the fuel under investigation, avoiding contamination of the crucible contents. The drops of fuel are introduced through the port (8), which is closed immediately after the drop has passed to prevent circulation of air or combustion products between crucible and atmosphere.

The fuel is discharged from an inclined burette which is protected from the radiation of the furnace by an asbestos sheet (9). The drop passes through a small hole which is closed by means of a sliding cover (10).

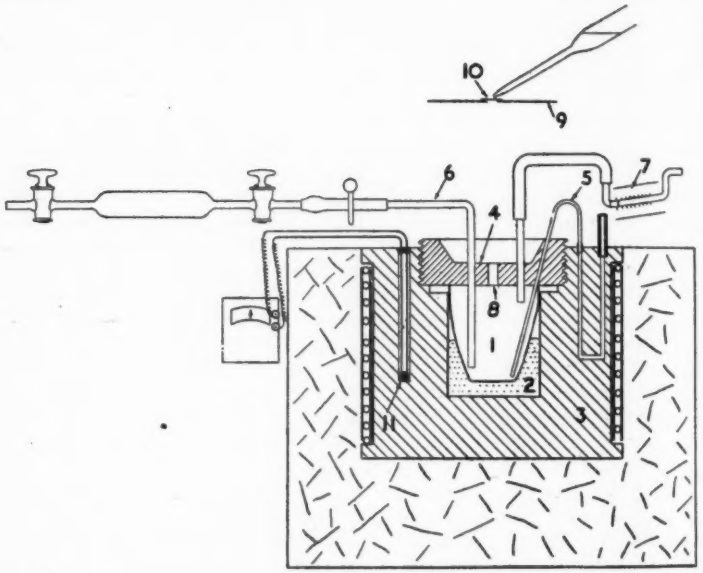


FIG. 1.

The temperature is measured with a nickel–nickel chromium thermocouple (11) and can be regulated by two resistances providing coarse and fine adjustment.

EXPERIMENTAL PROCEDURE FOR MEASURING IGNITION DELAYS.

A series of temperature–time-lag measurements were taken at falling temperatures, the resistances being so adjusted that the temperature dropped very slowly at less than 1° C a minute, permitting ample time for the measurements.

Before taking time-lag measurements, the crucible was " sensitized " by approximately 20 ignitions, which was found necessary to ensure consistent results. After each measurement the crucible was thoroughly scavenged

of the products of combustion and 2 minutes interpassed before the next time-lag measurement.

Two stop-watches were used to measure pre-ignition pulse and ignition time lags. The watches were started at the moment the drop left the burette. Time lags thus measured were corrected for the time interval of about 0·15 sec necessary for the drop to reach the bottom of the crucible.

Sampling and Analyses of Gas Mixtures.

For gas sampling the crucible was kept at a constant temperature. When frequent pre-ignition pulse or ignition time lags at that temperature had shown a constant value, a gas sample was withdrawn from the crucible. For each temperature, samples were taken at different stages of the reaction.

The gas samples are drawn from the crucible into an evacuated sampling tube of 17 cc capacity, through a Pyrex capillary which reaches to within 0·5 cm of the crucible bottom. The evacuated sampling tube is connected to the capillary by a short rubber sleeve, closed by a pinchcock. At the appropriate moment of sampling, the pinchcock is pressed and the sampling tube fills immediately. The sampled gases are chilled by keeping the sampling tube at a temperature of approximately 8° C.

The contents of the sampling tube were analysed for CO_2, O_2, unsaturated hydrocarbons, and CO in a modified Haldane Gas Analysis apparatus.

For the quantitative estimation of aldehydes, oxides of nitrogen, and peroxides separate gas samples were collected. The contents of the sampling tube were, by displacement with mercury, slowly bubbled through distilled water of 8° C at a rate of 1 bubble per second. The water had been boiled to destroy micro-organisms which might interfere with the determination of the oxides of nitrogen. (A special bubbler having a column of 12 cm height and a capacity of 10 cc was developed for this purpose.) 5 cc of this water were used for the estimation of aldehydes, 2 cc for oxides of nitrogen and 2 cc for peroxides.

Aldehydes.

The aldehydes were estimated colorimetrically, using Schiff's reagent (0·5 g of Fuschsin dissolved in H_2O added to 5 g of SO_2 dissolved in 500 cc of H_2O made up to 1000 cc with water and allowed to stand until colourless). Three drops of this were added to 5 cc of the extraction water. The samples were compared in special narrow Nessler glasses with standards of acetaldehyde. These standards were prepared at the same time as the samples, and the colorimetric determination was made 1 hour after their preparation, when the coloration did not show any further change. During this time the samples and standards were kept in tightly corked small test tubes.

Oxides of Nitrogen.

These were determined colorimetrically with Griess' Reagent. (Solution No. 1 : 1 g of sulphanilic acid to 14·7 g of glacial acetic acid and 15 ml of water, after dissolving and warming diluted with 300 ml water. Solution No. 2 : 0·2 g of α-naphthylamine added to 14·7 g of glacial acetic acid and 25 ml water. After dissolving and warming diluted with 300 ml water. Equal volumes of Solution 1 and 2 mixed immediately before use.)

2 cc of Griess' Reagent and 2 cc of distilled water were added to 2 cc of the extraction water. The samples were compared in special narrow Nessler glasses with standards of sodium nitrite prepared at the same time as the samples.

Colorimetric comparison was made after 3 hours, when the full colour had appeared.

Peroxides.

As NO_2 was found to be present only in small concentrations (as will be explained later), a relatively simple method for the peroxide determination could be adopted. This was especially helpful as, owing to the fact that the organic peroxides could be detected only within a small time interval, many sampling experiments and analyses were necessary to " catch " them. The method followed was first to take preliminary gas samples over relatively long time intervals. Once the presence of peroxides at a given stage of the reaction had been revealed, a number of samples within very small time intervals during this stage were taken.

The peroxides were determined with acid KI solution (2 cc of 5 per cent KI, 18 cc of water, 4 cc of $2N$-H_2SO_4, 1 cc of 1 per cent starch).

2 cc of the contents of the bubbler were quickly transferred to a special test tube through which nitrogen was being bubbled. To this were added 2 cc of the acid KI solution and 1 drop of 20 per cent ammonium molybdate. The test tube was then tightly stoppered. The blue colour developed very slowly after standing for approximately 1 hour.

A blank consisting of 2 cc distilled water, 2 cc of acid KI solution, and 1 drop of 20 per cent ammonium molybdate was prepared at the same time. After 2 hours standing the sample was titrated with 0·001N-thiosulphate using a micro-burette. During the titration nitrogen was again bubbled through the test tube. A correction was obtained by titrating the blank in the same manner. Tests were made as to the nature of the peroxides found. 1 drop of ferrous sulphate was added instead of ammonium molybdate. This, however, did not produce any colour, nor did KI by itself, without any catalyst, show any coloration, and it may be concluded that the peroxides found were of the mono-alkyl type.[11]

Experimental Results.

Experiments were carried out with n-heptane, mixtures of n-heptane and benzene, and n-heptane containing various amounts of tetra-ethyl lead.

Mixture Strength.

Before reporting the results it is necessary to discuss the conditions of mixture strength under which the experiments were carried out. The silica crucible used in the experiments had a volume of 60 cc. The volume of air reduced to N.T.P. contained in the crucible is different at different temperatures, decreasing with increasing furnace temperature. Varying amounts of air received therefore a *constant* weight of fuel and an increase in temperature corresponds to an increase, however small, in mixture strength. In order to establish the degree of variation over the temperature range investigated, the weight of the fuel drops was determined and found to be

0·0077 g for *n*-heptane and 0·0125 g for a mixture of 50/50 by vol *n*-heptane and benzene. From these results and the known air content of the crucible, the mixture strength for the different temperatures was calculated. Fig. 2 shows the variation with temperature of the mixture strength of *n*-heptane and 50/50 by vol *n*-heptane–benzene mixture.

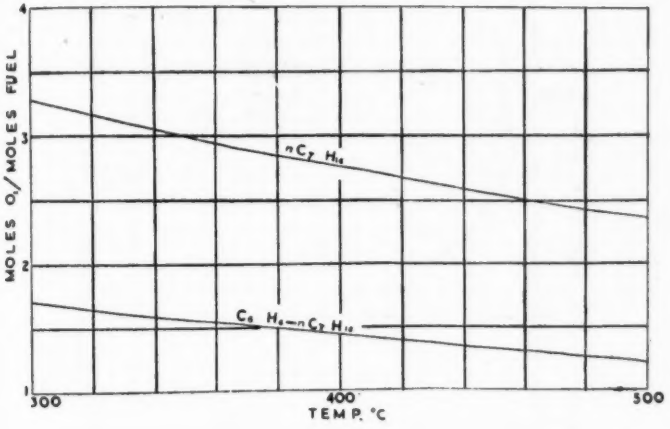


FIG. 2.

Results of Ignition Experiments.

During the preliminary experiments it was found that variation of ignition delays at constant temperature was to a great extent dependent on the barometric pressure. In the critical region in which two-stage ignition (pre-ignition pulse followed by ignition) may change to a pulse only (not followed by ignition), the barometric pressure seems to determine which of these two processes occurs, ignition being favoured by higher barometric pressure. The experiments were therefore carried out at barometric pressures as near as possible to 760 mm Hg, with a margin between different experiments of no more than 3 mm Hg.

n-*Heptane.*

Fig. 3 shows the delay–temperature curve of *n*-heptane.
Three definite regions can be distinguished on the graph :—

(*a*) A region above 400° C in which only ignition occurred. If a time interval exists between pre-ignition pulse and ignition, it was smaller than the lower limit of time measurable in the experiments which was of the order of ± 0·05 sec.
(*b*) A temperature range between 316° and 400° C in which two-stage ignition was observed. In this range a pre-ignition pulse is followed by ignition after a measurable time interval.
(*c*) Below 316° C no ignition could be observed. The pre-ignition pulse still occurs and becomes stronger with decreasing temperature.

The duration of the time interval between the pre-ignition pulse and ignition does not decrease with increase in temperature, but varies in this critical region, a fact also observed by A. Sokolik and S. Jantovski.[12] These workers distinguished two delays, the first τ_1, between the introduction

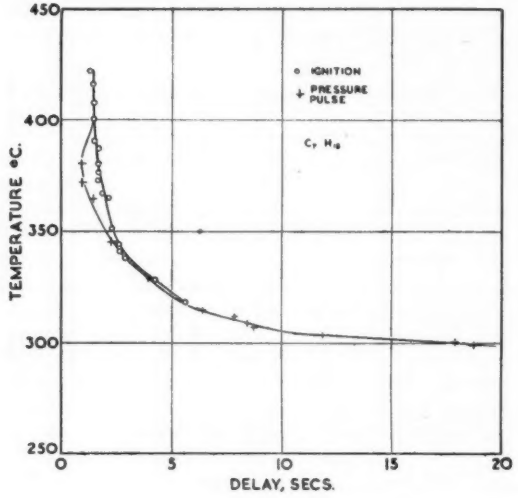


FIG. 3.

DELAY-TEMPERATURE CURVE OF *n*-HEPTANE.

of the charge into the reaction vessel and a small pre-ignition pulse, and a second delay τ_2, between the pressure pulse and ignition. They found that τ_1 decreases with increasing temperature (at constant pressure) and τ_2

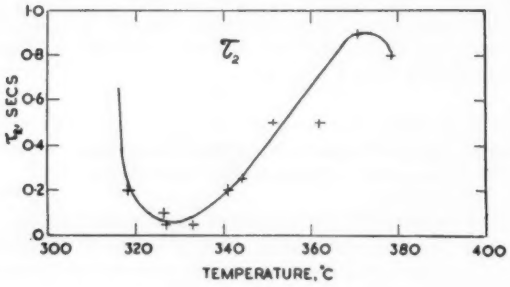


FIG. 4.

passes with increasing temperature first through a minimum and then through a maximum. Our experiments confirm some of the findings of Sokolik and Jantovski. As shown in Fig. 4 the time lag between pre-ignition pulse and ignition passes through a minimum at about 328° C,

whilst Sokolik and Jantovski report a minimum of τ_2 at 340° C and 1·5 atm. It is, of course, difficult to decide whether the difference is purely a pressure effect or may be due to differences of apparatus and experimental procedure.

n-Heptane–Benzene Mixtures.

The results of the ignition experiments with a *n*-heptane- benzene mixture (50/50 by vol) are reproduced in Fig. 5.

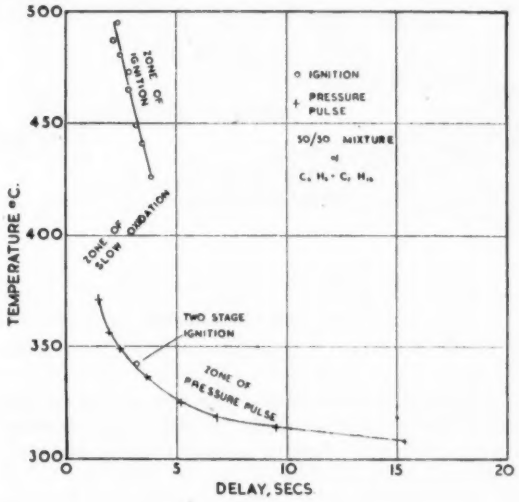


FIG. 5.

Three distinct temperature ranges can be distinguished :—

(*a*) Above 425° C normal ignition, possibly by a single stage mechanism.
(*b*) Between 370 and 425° C there is a zone in which only slow oxidation occurs. No pressure pulse could be observed in this range.
(*c*) Below 370° C a pre-ignition pulse occurs, which is not followed by ignition. Only at 324° C at a barometric pressure higher than 765 mm Hg was two-stage ignition observed with τ_2 having a very small value.

An interesting observation is the shortening of the time lags as one descends from the region of higher to that of lower temperature. For example, whilst the ignition delay at 425° C is 3·9 sec, the pre-ignition pulse at 370° C occurs after 1·5 sec, which seems to indicate a difference in chain mechanism in the different temperature ranges.

Tetra-ethyl Lead in n-*Heptane.*

Extensive measurements were carried out on solutions of tetra-ethyl lead in *n*-heptane, varying in concentration from 0·006 to 0·05 per cent by volume. The addition of tetra-ethyl lead increased the length of the delay

τ_1 only to a very small extent, but influenced the delay τ_2 considerably. The effects of temperature and tetra-ethyl-lead concentration on the ignition properties of *n*-heptane are illustrated in Fig. 6, which four regions can be distinguished.

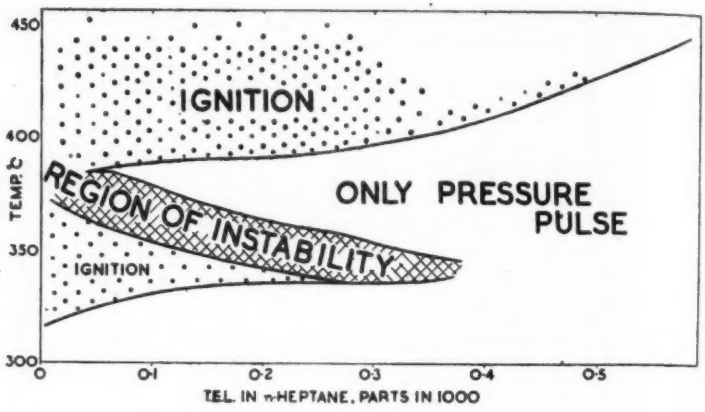


FIG. 6.

(*a*) A region above 380° C in which ignition occurs in the ordinary way, and which extends into relatively high concentrations of tetra-ethyl lead, though at slightly increasing temperatures.

(*b*) A wedge-shaped region beginning at about 380° C at 0·1/1000 T.E.L., and widening to a temperature interval between 350° and 400° C at 0·4/1000 T.E.L., in which only a pressure pulse could be observed.

(*c*) A region of "instability" between 350° and 400° C, the lower temperature corresponding to higher T.E.L. concentrations, in which either ignition or pressure pulse occurs.

(*d*) An ignition peninsula between 320° and 370° C at very low T.E.L. additions, but quickly disappearing with increasing T.E.L. in which ignition and pressure pulse occur.

The intensity of the pressure pulse obtained with the tetra-ethyl lead additions varied considerably. Even when the temperature was rigidly kept constant over a long period of time, the strength of the pulse varied between a very small indication on the manometer to the full intensity, comparable to that obtained with pure *n*-heptane.

Pre-ignition Pulse and Action of Anti-knocks.

Fig. 7 shows the time–temperature relationship of the pre-ignition pulse for *n*-heptane, *n*-heptane–benzene mixtures, and 1°/$_{oo}$ tetra-ethyl lead in *n*-heptane. Whilst a slight shift of the curve into a region of higher temperature can be observed, the shape of the curves is identical and no fundamental break in the curves is evident in the presence of anti-knocks.

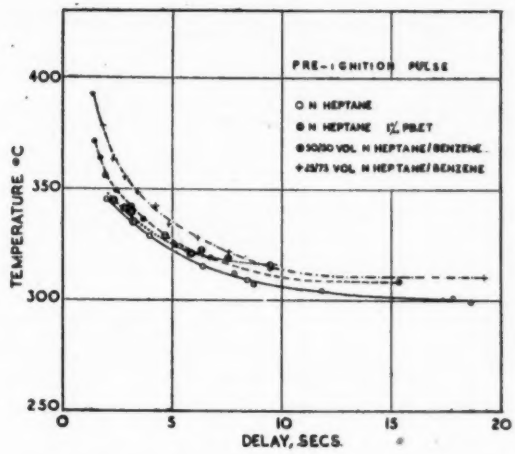


FIG. 7.

Composition of Gases during the Reaction.

As already mentioned, gas samples were withdrawn from the crucible at different stages of the reaction, a new drop charge being used for every sample. The analytical results for experiments with *n*-heptane at three temperatures and 50/50 *n*-heptane–benzene at two temperatures are given in Figs. 8, 9, 10, 11, and 12.

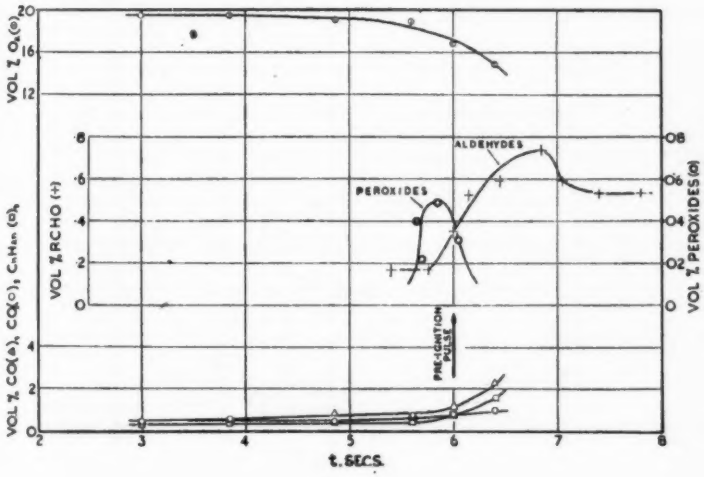


FIG. 8.

C_7H_{16} AT 316° C.

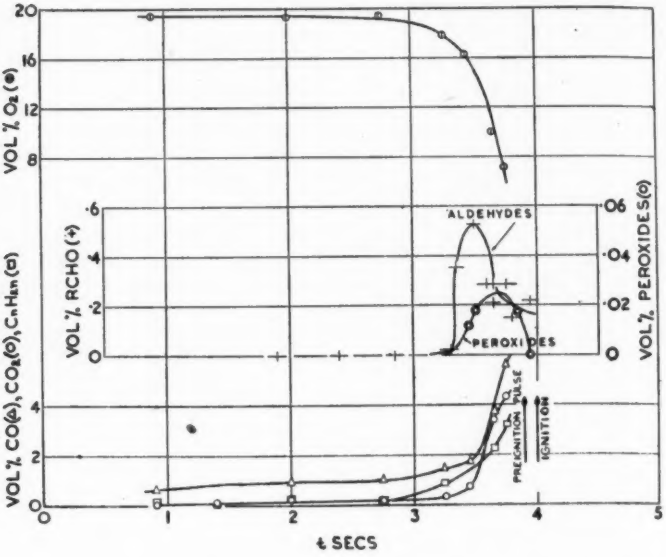


FIG. 9.

C_7H_{16} AT 327° C.

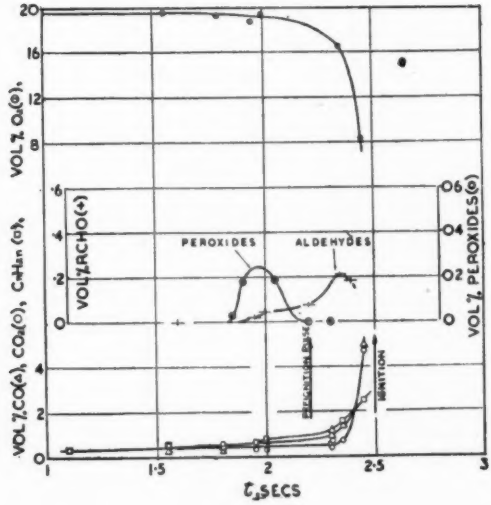


FIG. 10.

C_7H_{16} AT 345° C.

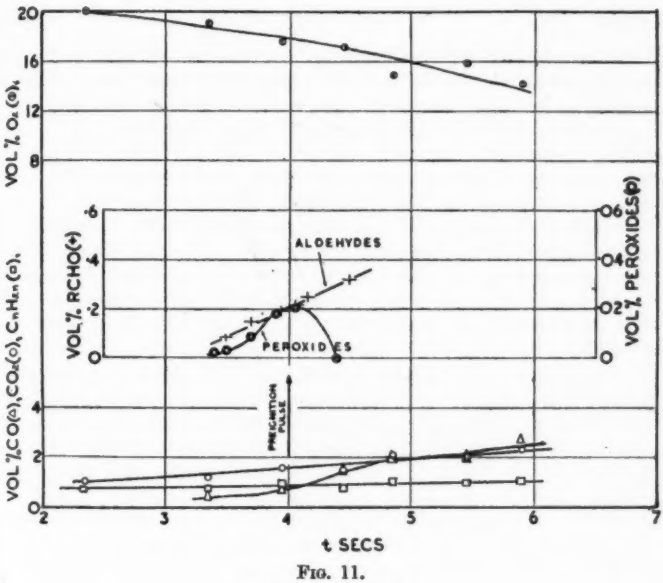


FIG. 11.

C_6H_6–C_7H_{16} AT 332° C.

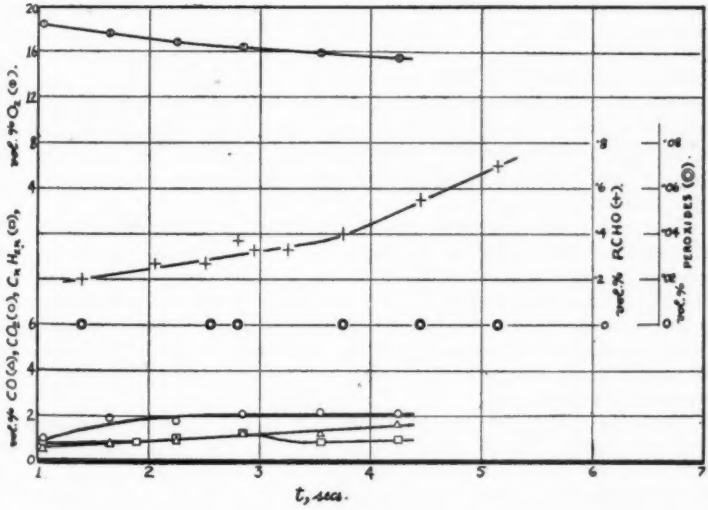


FIG. 12.

C_6H_6–nC_7H_{16} AT 386° C.

n-*Heptane.*

All curves obtained with *n*-heptane have certain features in common. Before a physical manifestation of the chemical reaction occurs, such as a pre-ignition pulse or ignition, oxidation reactions are proceeding, as shown by the presence of CO, CO_2, and C_nH_{2n} in the gas mixture. At a certain stage of the reaction peroxides appear in concentrations which allow determination by analytical methods. The concentration of peroxides increases to a maximum and then declines. *In the three cases shown, decline of the maximum concentration of peroxide coincides with the occurrence of the pre-ignition pulse.* This observation is in agreement with results obtained by previous workers. M. Brunner [13] observed a pressure increase in a *n*-heptane–oxygen mixture which occurred at the same instant at which a peroxide maximum began to decline. B. V. Aivazov and M. B. Neumann [14] observed that a pressure pulse occurred in *n*-pentane–oxygen mixtures, but only one set of results for a gas mixture at 318° C and 300 mm Hg is reported. Again the pressure pulse occurs simultaneously with the peroxide maximum. Whereas Brunner could not detect any aldehydes, Aivazov and Neumann found great amounts of aldehydes, and observed also that *the pressure pulse was followed by the appearance of a cool flame,* which can, of course, be ascribed to excited formaldehyde molecules.

The analysis of the gas mixtures obtained in the present work shows that the appearance of large amounts of aldehydes is connected with the presence of peroxides. The aldehydes, which may mainly consist of formaldehyde, accumulate to a maximum, which declines to a constant concentration. The relative position of the peroxide and aldehyde maxima indicates which of these two classes of compounds appear first in the chain mechanism which governs the sequence of events in the gas mixture. Both at a lower temperature (316° C, Fig. 8) and at a higher temperature (345° C, Fig. 10), the peroxide maximum occurs earlier than the aldehyde maximum. This leads to the conclusion that *aldehydes are more likely to result from the decomposition of peroxides* than *vice versa.* At 327° C (Fig. 9) the two maxima occur at practically the same instant, and this temperature is characterized by an extreme reactivity of the gas mixture, since the pre-ignition pulse is almost immediately followed by ignition, which occurs with great violence.

From the point of view of chemical kinetics, it is important to decide whether the decomposition of peroxides is immediately followed by an increase in concentration of the ultimate products of the reaction, namely CO, CO_2, and unsaturated hydrocarbons. Fig. 10 (345° C) reveals that this is not the case. There is, at this temperature, a relatively large delay between pre-ignition pulse and ignition, and only at the end of this time interval is there a significant increase in CO, CO_2, and C_nH_{2n} which leads eventually to ignition.

After the aldehyde concentration has passed through a maximum, ignition occurs. These observations lead to the conclusion that the peroxides are the intermediary compounds, whose stability and rate of decomposition at various temperatures govern the final chain reactions in the gas mixtures.

n-Heptane–Benzene Mixture (50/50 *by vol*).

The results at 332° and 386° C are given in Figs. 10 and 11. 332° C is within the temperature range which is characterized by pre-ignition pulse without ignition. As with pure *n*-heptane the pre-ignition pulse coincides with a decline of the peroxide maximum. The increase in aldehyde concentration was not followed up to its maximum. 386° C falls within the temperature range in which no physical manifestations such as pre-ignition pulse or ignition could be observed. Contrary to the previously described experiments, no peroxides could be detected. Aldehydes are formed at a much earlier stage of the reaction and their concentration increases continuously with time. The concentration of ultimate products CO, CO_2, and C_nH_{2n}, was found to increase very slowly.

Tetra-ethyl Lead in n-*Heptane*.

A series of gas sampling experiments was made with mixtures of tetra-ethyl lead in *n*-heptane. By the usual analytical procedure, the presence of the same reaction products such as peroxides, aldehydes, CO_2, CO, and C_nH_{2n} was ascertained. It was, however, found impossible to correlate their concentration with the stage of the reaction due to seemingly uncontrolled fluctuations in the intensity of the reaction. The fact that under rigorously constant conditions tetra-ethyl-lead solutions gave varying intensity of the pressure pulse is consistant with the lacking correlation of the analytical data.

The Presence of Oxides of Nitrogen.

The occurrence of oxides of nitrogen in oxidation reactions which are carried out with air is a well-established fact.[15] Egerton [16] and his collaborators found considerable amounts of nitrogen peroxide in the gases sampled from engine experiments. Since oxides of nitrogen may interfere with the analytical estimation of alkyl peroxides, their quantity in the reaction gas was determined. Table I gives the *maximum* concentration of oxides of nitrogen encountered in different experiments.

TABLE I.

Fuel used.	Temperature, ° C.	Maximum volume per cent of oxides of nitrogen.
n-Heptane	316	3×10^{-4}
n-Heptane	327	$1{\cdot}7 \times 10^{-4}$
n-Heptane	345	$1{\cdot}7 \times 10^{-3}$
n-Heptane–benzene . . .	332	$1{\cdot}7 \times 10^{-4}$
n-Heptane–benzene . . .	386	5×10^{-4}

These figures show that in the present experiments oxides of nitrogen did not influence the analytical estimation of peroxides to any great extent, since they were present only in very small amounts (about 1/100 of the concentration of peroxides).

The figures given in Table I are maximum concentration oxides of nitrogen

observed. As the reaction proceeded, the concentration declined, indicating that the oxides of nitrogen were consumed in the course of the reaction.

The presence of oxides of nitrogen in the reaction mixture seems to be connected with a direct reaction between nitrogen and oxygen. By means of Nernst's equation,[15] the equilibrium concentrations of NO in air were calculated, and are given in Table II.

TABLE II.

Temperature, ° C.	Equilibrium concentration NO in air, vol per cent (calculated).
300	3×10^{-4}
350	$1{\cdot}4 \times 10^{-4}$
400	$5{\cdot}1 \times 10^{-5}$

Comparing the figures in Tables I and II, one finds that the maximum concentrations of oxides of nitrogen are more than ten times higher than the equilibrium concentration of NO at the corresponding temperatures. This may suggest an oxidation mechanism between NO and some oxygen carrier, which has its origin in the hydrocarbon reaction, leading to the formation of NO_2, but there is not sufficient evidence to assume that oxides of nitrogen are the result of some chain terminating mechanism. Their disappearance towards the end of the hydrocarbon reaction indicates that they re-enter the chain at a later stage, which leads to their ultimate destruction.

THE CHAIN MECHANISM OF OXIDATION OF HIGHER PARAFFINS.

The most widely accepted theories on this subject are those put forward by A. R. Ubbelohde [17] and by B. Lewis and G. von Elbe.[3] Whilst a certain amount of agreement exists as regards the main reactions, nothing definite is known about the initiation of the chain reaction. Another important point which has hitherto attracted little attention is the fact that the oxidation of saturated paraffins is accompanied by the formation of *unsaturated hydrocarbons*. In the following the probable mechanism of oxidation of a straight-chain paraffin, such as *n*-heptane, will be discussed.

Initiation of Chain Reaction.

Lewis, von Elbe, and Ubbelohde (the latter using and amplifying the reaction scheme proposed by Backstrom [18]) assume that initiation proceeds through the formation of aldehyde molecules in a surface reaction. The main arguments in favour of this assumption are the observed facts that the induction period depends to a large extent on the nature of the surface of the reaction vessel, and that addition of small amounts of aldehydes reduces or even eliminates the induction period. It is, therefore, of interest to discuss the thermal changes which may occur in the formation of an aldehyde molecule from a saturated paraffin by an oxidation reaction. Such a reaction might be represented as in equation (1).

$$R{\cdot}CH_2CH_3 + O_2 \xrightarrow{\text{Surface}} R{\cdot}CH_2CHO + H_2O \quad . \quad . \quad (1)$$

The heat balance of reaction (1) is as follows :—

The dissociation of the oxygen molecule and the breaking of two C—H bonds require about 316 kcal. From the formation of water and the C=O bond about 270 kcal are available. The reaction is, therefore, endothermic by about 46 kcal. In the activated complex of the reaction three bonds are involved, which suggests a high energy of activation for the reaction. It is, therefore, unlikely that the formation of an aldehyde molecule represents the initiation of the hydrocarbon oxidation chain.

An alternative mechanism suggests itself readily. It is known that the cracking reaction of hydrocarbons is induced by the presence of oxygen under conditions under which it would normally not take place. Since the pyrolysis of hydrocarbons is obviously connected with the formation of free alkyl radicals, one may conclude that the presence of oxygen increases the probability of such radicals being formed from the paraffin hydrocarbons.

$$C_nH_{2n+2} + O_2 \begin{cases} \nearrow C_nH_{2n+1}^{\cdot} + HO_2 \quad . \quad . \quad . \quad (2) \\ \searrow C_nH_{2n}^{\cdot\cdot} + H_2O_2 \quad . \quad . \quad . \quad (3) \end{cases}$$

Reactions (2) and (3) are exothermic by 11 and 22 kcal respectively. Only one or two bonds are involved in the activated complex of the reaction so that the energy of activation is not likely to be excessive. HO_2 may interact with another hydrocarbon molecule to give a radical and H_2O_2. The presence of H_2O_2 has been suggested by E. J. Harris and A. Egerton.[19] The existence of $CH_3^{\cdot}$ and $C_2H_5^{\cdot}$ radicals at temperatures between 700° and 1000° C has been shown by F. O. Rice.[20] It is likely that at lower temperatures higher radicals than those found by Rice may exist. The radicals $C_nH_{2n+1}^{\cdot}$ and $C_nH_{2n}^{\cdot}$ may now undergo polymerization reactions, as shown in equations (4) and (5).

$$2C_nH_{2n+1}^{\cdot} \longrightarrow C_{2n}H_{4n+2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Reaction (4) produces a higher paraffin, which, however, is less stable than the original paraffin and is likely to form free radicals again when colliding with an oxygen molecule.

$$2C_nH_{2n}: \longrightarrow C_nH_{2n} :: C_nH_{2n} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

A collision between two divalent alkyl radicals may therefore result in the formation of an olefine which, after stabilization, will form part of the products of the overall reaction.

The position of the "odd electrons" on the alkyl radicals must be discussed in order to define the controversial question of "oxygen attack." In the mild pyrolysis of straight-chain paraffins, branched-chain paraffins may be formed. This reaction, which forms the basis of the industrial process of "isomerization," suggests that the first point of attack occurs along the hydrocarbon chain and not in the terminal CH_3 groups. The products of the initiation reaction are, therefore, likely to be secondary alkyl radicals, as suggested by A. D. Walsh.[21] A univalent radical of this

type can be represented by the formula RCHR′, where R and R′ may be of about equal chain length.

The Primary Chain Reaction.

The alkyl radical RCHR′ by collision with O_2 will form a secondary alkyl peroxide radical.

$$R\dot{C}HR' + O_2 \longrightarrow RCHR' \quad . \quad . \quad . \quad . \quad . \quad (6)$$
$$\qquad\qquad\qquad\qquad\qquad\quad O$$
$$\qquad\qquad\qquad\qquad\qquad\quad \dot{O}$$

The peroxide radical in colliding with a paraffin molecule will restart the chain under the formation of a secondary alkyl hydrogen peroxide.

$$\begin{matrix} RCHR' \\ O \\ \dot{O} \end{matrix} + RCH_2R' \longrightarrow R\dot{C}HR' + \begin{matrix} RCHR' \\ O \\ O \\ H \end{matrix} \quad . \quad . \quad . \quad (7)$$
$$\qquad\qquad\qquad\qquad\quad \downarrow$$
$$\qquad\qquad\qquad\qquad \text{Repeats the chain.}$$

The fate of the secondary alkyl–hydrogen-peroxide molecule determines the further course of the reaction.

The Decomposition Reaction of the Secondary Peroxide.

The formation of a secondary in preference to a primary alkyl–hydrogen peroxide has been postulated by A. D. Walsh,[20] who on the basis of this hypothesis, rejects the theories put forward by Lewis and von Elbe. It can, however, be shown that " oxygen attack " on a secondary carbon atom in preference to a primary is quite consistent with the reaction scheme proposed by Lewis and von Elbe. In fact it allows for a combination of their reaction scheme with that proposed by Ubbelohde. The most likely reaction the secondary peroxide undergoes is unimolecular decomposition.

$$\begin{matrix} R{-}CH{-}R' \\ \quad O \\ \quad\vdots \\ \quad O \\ \quad H \end{matrix} \longrightarrow RCHO + R\cdot' + \cdot OH \quad . \quad . \quad . \quad (8)$$

It is to be noted that 3 units are formed from the decomposition of one molecule.

The ·OH radical generates a new primary chain when colliding with a paraffin molecule, according to

$$R\,CH_2R' + \cdot OH \longrightarrow R\dot{C}HR' + H_2O \quad . \quad . \quad . \quad (9)$$
$$\qquad\qquad\qquad\qquad\quad \text{Repeats primary chain.}$$

In the present scheme ·OH radicals are considered to be the main chain carriers. The aldehyde molecule and the primary alkyl radical follow their respective reaction schemes which will be discussed below.

Degradation of Aldehydes and of Primary Peroxides.

The aldehyde molecule formed in reaction (8) may undergo the degradation reaction scheme proposed by Lewis and von Elbe.

$$RCHO \xrightarrow{\text{radical}} RCO \xrightarrow{O_2} CO + H_2O + R''CO$$
$$\xrightarrow{O_2} \ldots\ldots \xrightarrow{O_2} HCHO^* + CO + \cdot OH \quad . \quad . \quad (10)$$

A certain proportion of aldehyde by surface reaction will be oxidized to CO_2 and H_2O.

The primary radical R·′ may give rise to a *primary* peroxide radical, which may follow the degradation scheme proposed by Ubbelohde

$$R\cdot' \xrightarrow{O_2} R'OO\cdot \xrightarrow{R\text{-}CH_2R'} R'OOH \longrightarrow R'O\cdot + \cdot OH$$
$$R'O\cdot \xrightarrow{O_2} R'''\text{—}O\text{—}O\cdot + HCHO \quad . \quad . \quad . \quad . \quad (11)$$

The reaction schemes (10) and (11) occur simultaneously. The final reaction of (10) is exothermic by 110 kcal and produces HCHO in a state of excitation. The final reaction of (11) is exothermic by 22 kcal, which is not sufficient to produce HCHO above its ground state. The fact that HCHO is the product of two reaction schemes may account for only a fraction of the formaldehyde present being in a state of excitation [22] (giving rise to " cool flames ").

The Branching Reaction.

Lewis and von Elbe account for the branching reaction by the interaction of a primary peroxide radical and an aldehyde molecule. This gives rise to an oxy-dialkyl peroxide.

$$R'OO\cdot + RCHO \longrightarrow R'OOC(OH)R \quad . \quad . \quad . \quad (12)$$

The branching reaction is then said to follow the following scheme :—

$$R'\text{-}OO\text{-}C(OH)\text{-}R \longrightarrow R'O\cdot + RCO\cdot + \cdot OH$$
$$\downarrow O_2 \qquad \downarrow O_2$$
$$2\cdot OH + R''CO \qquad \rightarrow \ldots\ldots HCHO^* + CO + \cdot OH \quad (13)$$
$$\downarrow O_2$$
$$\rightarrow \ldots\ldots HCHO^* + CO + \cdot OH$$

The reaction scheme (13) implies intensive branching five ·OH being formed from the decomposition of a single molecule of oxy-dialkyl peroxide.

Perhaps the strongest evidence in favour of the mechanism put forward is given by the work of Dumanois, Mondain-Monval, and Quanquin.[23] With mixtures of higher paraffin hydrocarbons and air at 200° C, these workers observed only a slight formation of aldehydes and carbon dioxide. At 325° C heavy white fumes were found to form, which are probably identical with the reactive vapours expelled during the pre-ignition pulse. On condensing the fumes two liquid layers were obtained. The aqueous layer contained large amounts of formaldehyde while the oily layers, on distillation *in vacuo*, yielded a yellowish oil which showed characteristic reactions of

alkyl peroxides. This oil, on heating to 200° C, decomposed with the formation of a " cool flame " and liberation of aldehydes.

Recently Walsh [24] discussed the reactions occurring during the oxidation of paraffin hydrocarbons. The conclusions reached with regard to initiation, the formation of secondary peroxides and their decomposition are in agreement with the scheme proposed in this paper up to reaction (8). With respect to the branching reaction, and particularly the formation of excited formaldehyde, Walsh is at variance with Lewis and von Elbe, pointing out many weaknesses in their reaction scheme. We feel, however, that Walsh has not produced an alternative scheme to explain the extensive branching reaction, which necessarily is the cause of ignition.

Application of the Theory to the Experimental Results.

The experimental results shown in Figs. 8–10 show one important fact. *In all experiments the " pre-ignition pulse " occurred immediately after the peroxide maximum.* The observations relating the pre-ignition pulse to gas composition may be summarized thus :—

(*a*) The " pre-ignition pulse " coincides with a decline in alkyl–hydrogen peroxide concentration (since only this type of peroxide was measured by the analytical procedure adopted).
(*b*) It is normally connected with a rapid increase in aldehyde concentration.
(*c*) It is not accompanied by copious branching, since not in all cases does it lead to ignition.
(*d*) The observed rise in pressure is of the order of a few mm water gauge.

The partial pressure of the detectable peroxides in the gas mixtures at the maximum concentration is of the order of 2 mm water gauge. Reaction (8), describing the decomposition of secondary alkyl hydrogen peroxides, results in the formation of three units from a single molecule. If the decomposition of the secondary alkyl–hydrogen peroxide was responsible for the " pre-ignition pulse " a pressure increase of about 4 mm water gauge may be expected to occur. This is within the order of magnitude of the observed pressure increase, and one may infer that the " *pre-ignition pulse " is due to the decomposition of secondary alkyl–hydrogen peroxides.*

It is now necessary to relate the behaviour of the explosive mixtures at different temperatures to the probable behaviour of the products of reaction (8). With *n*-heptane at 316° C it was observed that the " pre-ignition pulse " was followed by an increase in aldehyde concentration which did not lead to ignition. This suggests that the oxy-dialkyl peroxides are sufficiently stable at that temperature as to avoid rapid branching.

The occurrence of the " pre-ignition pulse " without ignition at 316° C may thus be explained by the greater instability of alkyl–hydrogen peroxides as compared with dialkyl peroxides. A. D. Walsh [25] pointed out that the bond strength in O–O differs considerably in these two types of compounds, due to charge transfer from the alkyl groups to the peroxidic bond.

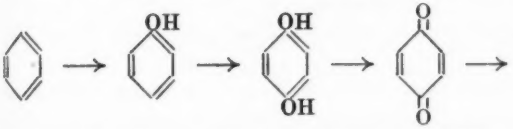
At 327° C the peroxide and aldehyde maxima were found to occur very

close to each other. The relative position of the maxima is almost reversed as compared with the results at lower and higher temperatures. Thus the decomposition of secondary alkyl peroxides, the formation and decomposition of oxy-dialkyl peroxides follow each other in rapid succession, and the " pre-ignition pulse " is rapidly followed by ignition.

At 345° C the di-alkyl peroxides are not formed since the primary peroxide radicals may be decomposed according to (11) before being able to react with an aldehyde molecule according to (12). The decomposition products of the " pre-ignition pulse " follow degradation reactions, which, however, are sufficiently rapid to lead to ignition, though after some delay. The possibility must also be considered that at this stage thermal branching may play some part. The thermal energy liberated during the degradation reactions, accumulating in the gas mixture may be sufficient to lead to a process of self acceleration of these reactions.

*The Mechanism of the Oxidation of Benzene-*n*-heptane Mixtures.*

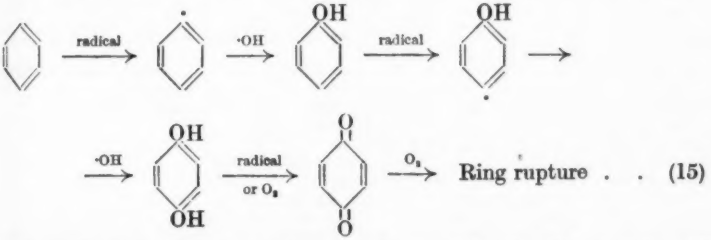
Very little is known of the mechanism of the oxidation of benzene. It probably proceeds by successive hydroxylation, followed by quinone formation and ring rupture.[26] R. Fort and C. N. Hinshelwood [27] found that



(14)

the rate of oxidation varied with a high power of the benzene concentration, indicating a chain mechanism.

In the presence of large amounts of benzene the oxidation reaction of *n*-heptane is likely to be strongly affected. The mechanism of the interference of benzene may be the following :—



(15)

According to scheme (15) benzene is very effective in removing 'OH radicals from the gas mixture. It is, therefore, likely to influence the branching reaction of *n*-heptane oxidation without interfering to a great extent with initiation or secondary peroxide formation. This is best illustrated by comparing the experimental results for *n*-heptane and benzene–*n*-heptane mixture at 330° C (Figs. 9 and 11). The peroxide maximum and the " pre-ignition pulse " occur after a delay of about 4 seconds in both experiments. In the experiment with pure *n*-heptane the " pre-ignition pulse " is followed almost immediately by ignition, indicating

copious branching. With the benzene–*n*-heptane mixture the "pre-ignition pulse" does not lead to branching and ignition, indicating that the chain carriers of the branching reaction (·OH) are efficiently removed from the gas mixture by the benzene molecules.

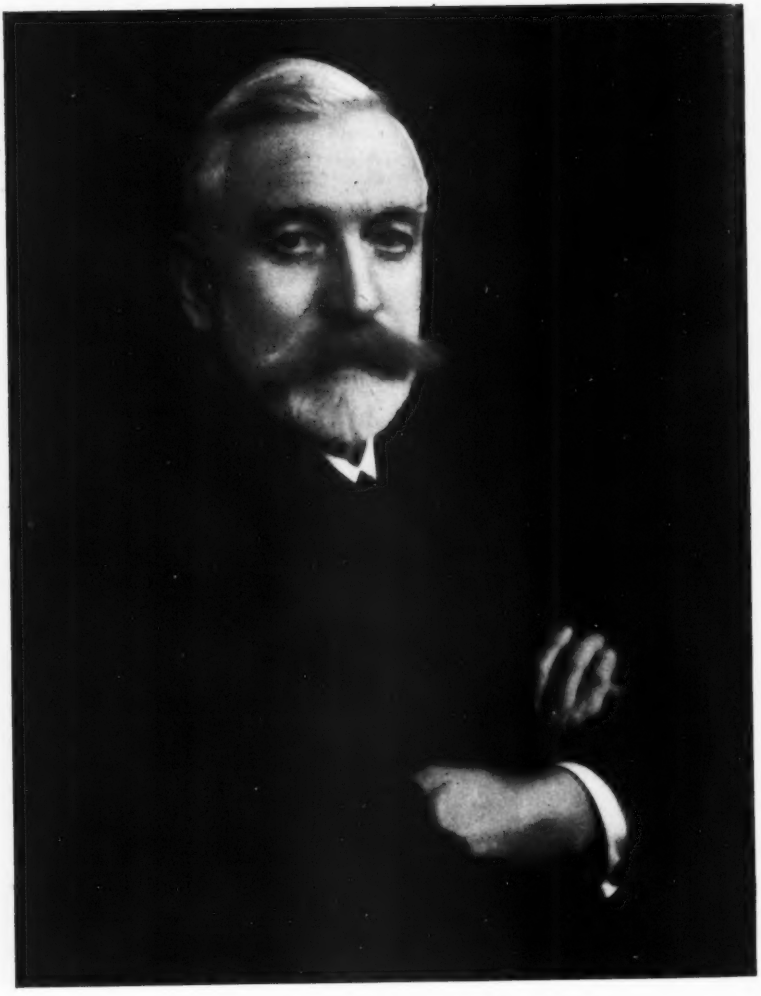
In the experiment with benzene–*n*-heptane at 386° C (Fig. 12) no "pre-ignition pulse" occurred and the presence of alkyl peroxides could not be detected. It is likely that this temperature corresponds to a region of instability of the peroxides. Coupled with this effect may be an increase in the oxidation reaction of benzene, which reduces the number of ·OH chain carriers available. The net result is, therefore, a slowing down of the overall combustion reaction.

Acknowledgements.

The authors wish to thank Dr Rosin Industrial Research Co. Ltd, in whose laboratory the experiments were carried out, for permission to publish this paper, and Dr P. O. Rosin personally for critically reviewing it. Thanks are also due to Mr. W. Guttmann for assistance rendered during the experiments.

References.

1 "Symposium on Gaseous Combustion" (*American Chemical Society*). *Chem. Rev.*, 1937, **21**, 209 ff.
2 "Science of Petroleum," 1938, Vol. 4, 2860 ff. (Oxford.)
3 "Combustion, Flames and Explosions," Lewis, B., and von Elbe, G. Cambridge 1938.
4 "Oxidation." *Trans. Faraday Soc.*, 1946, **42**, 99 ff.
5 Holm, H. *Z. angew. Chem.*, 1913, **26**, 273.
6 Moore, H. *J. Soc. chem. Ind.*, 1917, **36**, 110; *J. Instn Petrol. Tech.*, 1920, **6**, 186.
7 Sortman, C. W., Beatty, H. A., and Heron, S. D. *Industr. Engng Chem.*, 1941, **33**, 357.
8 Townend, D. T. A. *Chem. Rev.*, 1937, **21**, 259.
9 *e.g.*, Maccormac, M., and Townend, D. T. A. *J. Chem. Soc.*, 1940, 151.
10 Prettre, M. *Trans. Faraday Soc.*, 1946, **42**, 352.
11 Egerton, A. C., Smith, F. L., and Ubbelohde, A. R. *Phil. Trans. Roy. Soc.*, 1935, **234**, 433.
12 Sokolik, A., and Jantovski, S. *Acta Physico-chim.* (*U.R.S.S.*), 1944, **19**, 329.
13 Brunner, M. *Helv. Chim. Act.*, 1928, **11**, 881.
14 Aivazov, B. V., and Neumann, M. B. *Acta Physico-chim.* (*U.R.S.S.*), 1937, **4**, 575.
15 *cf* Mellor, "Inorganic and Theoretical Chemistry," Vol. 8, Longmans.
16 Egerton, A., *et al.*, *Proc. Roy. Soc.*, 1935, **152**A, 354; 1936, **153**A, 113.
17 Ubbelohde, A. R. *Proc. Roy. Soc.*, 1935, **152**A, 354.
18 Backstrom. *Z. phys. Chem.*, 1934, **25**B, 99.
19 Harris, E. J., and Egerton, A. *Chem. Rev.*, 1937, **21**, 287.
20 Rice, F. O. *Trans. Faraday Soc.*, 1934, **30**, 152.
21 Walsh, A. D. *Trans. Faraday Soc.*, 1946, **42**, 269.
22 Topps, J. E. C., and Townend, D. T. A. *Trans. Faraday Soc.*, 1946, **42**, 345.
23 Dumanois, P., Mondain-Monval, P., and Quanquin, B. *Compt. Rend.*, 1930, **191**, 299.
24 Walsh, A. D. *Trans. Faraday Soc.*, 1947, **43**, 297.
25 Walsh, A. D. *Trans. Faraday Soc.*, 1946, **42**, 264.
26 Newitt, D. M. *Chem. Rev.*, 1937, **21**, 299; Newitt, D. M., and Townend, D. T. A. *Science of Petroleum*, 1938, Vol. IV, 2884. (Oxford.)
27 Fort, R., and Hinshelwood, C. N. *Proc. Roy. Soc.*, *A*, 1930, **127**, 218.



ALFRED COURTHOPE ADAMS, 1864–1948.

[*To face p.* 511.

OBITUARY.

ALFRED COURTHOPE ADAMS.

It is with deep regret that we report the death of Alfred Courthope Adams at Colchester on May 16, 1948. Mr Adams was a very well-known personality in the petroleum industry for a long number of years.

Mr Adams was born in 1864, the son of J. R. Adams, a solicitor, and was educated first at Dulwich College, London, and later privately at Bruges, Belgium. He first became connected with the oil industry on the Thames in 1881, and it can undoubtedly be said that he was the father of the industry in this region and lived to see his early efforts crowned with success.

Secretary of the original London and Thames Haven Petroleum Wharf Ltd., which was founded in 1894, he became a director of that company in 1897. When the company was incorporated as London & Thames Haven Oil Wharves Ltd., in 1898, he became its managing director, which position he held until 1919, when T. C. J. Burgess joined him as joint managing director. This association continued until 1938, when Mr Burgess retired and was replaced by A. E. Sawdy. Mr Adams resigned his position as joint managing director on his retirement due to ill health in 1940.

The conception and development of London & Thames Haven Oil Wharves Ltd., the first ocean installation to import petroleum in bulk into Britain, was largely due to Mr Adams' foresight, and he lived to see the company grow into one of the largest oil-storage installations in Europe.

During the 1914–18 war he was invited by the industry to be chairman of the Pool Board, which during that war was the equivalent of the Petroleum Board in the last war, and he acted in that capacity with conspicuous success during the whole of its operative life.

He was a Founder Member of the Institute when it was formed in 1913 as the Institution of Petroleum Technologists, a member of its first Council, and its President during the years 1927–29. He was chairman of the Finance Committee from the foundation of the Institute until 1933 and remained a member of the Committee until 1939. His advice was always welcomed for its soundness.

He had many outside interests, but perhaps the one to which he was most devoted was yachting, most of his week-ends between spring and autumn being spent on his yacht. For many years he was Commodore of the Royal Temple Yacht Club, and also a member of the Colne Yacht Club. He took a great interest in all matters regarding the Thames waterway and the adjacent lands, and his knowledge of the lower reaches of the Thames and its navigation problems was encyclopædic.

He served on the committee of H.M. Commission for Fobbing Levels, and for many years was a prominent member of the Essex Rivers Catchment Board.

It was these combined interests which conjointly led to his becoming a very well-known authority on Thames navigation.

Mr Adams was in disposition kindly and just, but withal a great

disciplinarian. He was well liked, respected, and trusted, and his passing will be deeply regretted by all those who knew and worked with him.

A. E. S.

WILLIAM A. PETERS, Jr.

Killed at Shannon, Ireland, April 15, 1948, in the crash of the Pan-American Airways plane " Empress of the Skies," W. A. Peters, Jr., vice-president and director of all foreign operations of E. B. Badger & Sons Company, was en route to Boston via London following an extended trip through South Africa.

Born in Seattle, Washington, on May 20, 1890, Mr Peters graduated from Yale in 1912 with an A.B. degree and received an M.S. (Mining) from the University of California in 1914. He was engaged in geological and survey work directly following his college training until 1915 when he started with the du Pont Company at their Parlin, N.J. plant. While there he developed improvements in handling waste nitro-cellulose and scrap powder, and a method of transporting partly finished powder by jetting through pipes with water. (This method was in use in large smokeless-powder plants of the second world war.) When the powder plants were closed he went into the chemical department at Wilmington and worked on various chemical-engineering problems at many of the du Pont plants, specializing particularly in distillation. In collaboration with T. Baker he developed a special arrangement of fractionating plate that has been used in a large number of installations.

W. A. Peters joined the Badger Company in 1924 to study the possibility of applying the plate type of fractionating equipment in the petroleum field and to represent the company on the Pacific Coast in this and other fields. He took charge of certain experiments then in progress at the company's Ann Arbor laboratory. This work resulted in the installation in 1925 of several small bubble-cap-type fractionating towers in petroleum refineries in Texas and Oklahoma and then in Pennsylvania and California, and represented the first general use of that type of equipment in the petroleum industry. It stands as a definite step in the progress of the industry.

In 1925 Mr Peters introduced Badger equipment to the Anglo-Persian Oil Company and in 1926 he went to Persia to supervise the installation and operation of the first unit. This unit was followed by others for Persia, England, Scotland, and Wales. In 1935 he designed for the same company the largest topping and vacuum plant ever built and put it into operation in 1936. He spent considerable time at The Hague in 1928 and 1929 in connexion with the units for Curaçao, and supervised construction and operation of Badger units in Russia in 1930 and 1931. In 1938 he was made a vice-president in particular charge of foreign work and subsequently set up two subsidiary companies in Great Britain and another in France.

Mr Peters directed the early operations in the development of vacuum distillation of lubricating oil. This work was the foundation for much of the vacuum-lube-oil equipment in present refineries. In 1928 he developed a system of vacuum fractionation for handling pressure distillates that resulted in wide application.

In World War II he had general charge of the Badger T.N.T. projects and

responsibility for their designs. He re-designed waste-disposal methods resulting in substantial economic advantage to the U.S. Government.

Mr Peters was the author or co-author of many articles on distillation. He became an Associate Member of the Institute of Petroleum in 1926 and was also a member of the American Chemical Society and the American Institute of Chemical Engineers among others.

Endowed with unique talents, possessed of unbounded energy and interest in human values and events, "Ole" Peters, as he was familiarly and affectionately called by his associates and friends, was peculiarly a part of the very fabric of the lives of those who were privileged to experience the impact of his keen mind and spirit. As a monument to his memory and an inspiration to those he left behind, there remain to-day many important projects which testify to his engineering genius and unflinching professional integrity.

To his widow and daughter we tender our deepest sympathy.

J. T. T. R.

WILLIAM ROBERT GUY.

William Robert Guy, who was on the chemical staff of Scottish Oils Ltd., died suddenly on the morning of June 24, 1948.

Born near Kilwinning, Ayrshire, in December 1894, he was educated at Kilmarnock Academy and the Royal Technical College, Glasgow. After a brief spell as lecture demonstrator to the late Professor G. G. Henderson at the Royal Technical College in 1917, he joined the Chemical Inspection Department at Woolwich Arsenal, where he remained until 1919. Before entering the shale industry, he was engaged for two years in paint manufacture at Preston. From 1921 to 1925 he was with the Pumpherston Oil Co., and when in the latter year Scottish Oils opened a Central Laboratory at Middleton Hall, Uphall, Mr Guy was appointed as chemist in charge, a post which he held at the time of his death.

He was elected an Associate of the Institute of Chemistry in 1919 and passed to the Fellowship grade in 1943. He became a Fellow of the Institute of Petroleum in 1939, and was closely associated with the activities of the Scottish Branch since its foundation, first as assistant secretary, and from 1946, when the Branch resumed its activities after the war, as secretary. His enthusiam for the Branch affairs was great and much of its success was due to his efforts and genial personality. He represented the Branch on the Council of the Institute from 1947, and took an active part in all its meetings, particularly as a member of the Branches Committee.

William Robert Guy had a cheerful and happy temperament, with a remarkable gift of friendship. He was always willing to help and advise and as a careful and capable teacher he was regarded by the numerous staff who came under his care with gratitude and respect. By his many colleagues and friends in the shale industry he was held in high esteem for his upright character and kindly consideration at all times.

Mr Guy leaves a widow and an only son, to whom we express our sincere sympathy.

R. C.